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(54) Title: HYDROPHOBIC MODIFICATION OF MINERAL FILLERS AND MIXED POLYMER SYSTEMS

(57) Abstract: A process for imparting hydrophobicity to a filler with a blend of a plurality of silanes, said process including admixing at least one mildly hydrophobic silane, at least one strongly hydrophobic silane, and at least one functional silane with said filler under controlled alkaline conditions.

HYDROPHOBIC MODIFICATION OF MINERAL FILLERS AND MIXED POLYMER SYSTEMS

FIELD OF THE INVENTION

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This invention relates to methods of treatment of particles, preferably mineral particles, to impart hydrophobicity thereto, and to uses of said treated particles including the production of moulded articles and the products produced by the aforesaid processes. In particular, this invention relates to methods of imparting hydrophobicity to particles intended to be used as fillers with epoxy-resins and other resins and polymers, the hydrophobically treated particles themselves, methods of use of the hydrophobically treated particles, and products, including moulded products, incorporating the hydrophobically treated particles. More particular aspects of the invention relate to methods of imparting hydrophobicity to silica particles, including silica flour, to the hydrophobically treated silica particles, to the uses of said hydrophobically treated silica particles, to products incorporating said hydrophobically treated silica particles, including tyres and electrical voltage insulators, and to methods of production of such products.

20

BACKGROUND AND INTRODUCTION TO THE INVENTION

The imparting of hydrophobicity to fillers is one means of altering the properties, such as the strength, of resultant products incorporating those treated fillers. An extensive number of patents disclose hydrophobic treatment of fillers, minerals and substrates with non-functional alkyl and fluoroalkyl silanes.

25

A number of diverse industries are referred to in those patents including cosmetics, electrographic, tyre, filled polymer systems and building/construction, not only in the field of electrical voltage insulators. The treatment systems used in these industries relate to specific applications such as a requirement to improve 'softness' for silica used in cosmetics, for example.

30

Electrical insulators traditionally have been made of glass or porcelain. However, these have suffered from a number of problems when compared to silica filled epoxy insulators. Problems have included greater weight, higher thermal coefficient of expansion, lower tensile, flexural, impact and compression strengths, poorer processing flexibility, poorer repairability, higher dielectric constant, slightly lower track resistance, slightly worse chemical resistance, and worse erosion and weathering properties. Water absorption is comparable when compared to hydrophobic epoxy systems.

10 Prior art resin insulators have proven to be deficient in arc track resistance, weatherability, impact strength or castability.

The most popular polymer resin insulator materials are the epoxies, silicone rubbers, urethanes, and ethylene propylene diene modified rubbers (EPDM).

15 The use of silicone polymer resins when compounded into insulators offers potentially greater durability than use of silica-filled epoxy insulators due to inherently better UV resistance. However, the strength and cost are normally prohibitive compared to silica filled epoxy systems and their use is limited.

20 Insulators made from epoxy polymeric materials containing silica filler (or silica flour) as a filler have been developed for use in high voltage installations.

25 British Patent No. 1303432, describes a method of improving the strength, durability and hydrophobicity in high voltage insulators wherein functional organic groups are specified on the silane molecule in the process of chemically treating the silica filler incorporated in the system.

30 Compared to silicone, porcelain and EPDM insulators, silica filled cycloaliphatic epoxy insulators can offer advantages in cost, weight, tracking, erosion resistance, maintenance requirements, flash over and corona resistance, design versatility and manufacturing complexity.

However, such insulators have demonstrated inconsistent performance particularly when hydrophobicity of the insulator is lost on exterior exposure leading to wetting of the surface to give a continuous sheet of water combined with
5 deposition of fillers and this can lead to a higher potential of electrical arcing occurring across the face of the insulator.

Cycloaliphatic epoxy resins are recommended in preference to the more common bisphenol based, aromatic epoxy polymers. Superior weathering and greater
10 durability is generally observed with the use of cycloaliphatic epoxy polymers compared to the aromatic polymer types. The cycloaliphatic resin types are particularly suitable for use in high voltage insulators compared to aromatic based polymers due to a reduced carbon deposit left on a tracking line when arcing occurs across the face of the insulator.

15 Suitable resins include all epoxy resins containing cycloaliphatic structural units including cycloaliphatic glycidyl compounds and β -methylglycidyl compounds. In particular hexahydrophthalic acid diglycidyl ester and 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate are preferred.

20 A range of epoxy hardeners can be used in this application. However, it is preferable to use cyclic carboxylic acid anhydrides or polyanhydride hardeners. These offer 100 % solids and superior durability compared to polyamine or polyamide hardeners commonly used for ambient cured epoxy resin based systems.

25 The isomeric mixtures of methyltetrahydrophthalic anhydride and tetrahydrophthalic anhydride are commonly used, as are, hexahydrophthalic anhydride and methylhexahydrophthalic anhydride.

30 Preferred accelerators are tertiary amines, in particular, benzyldimethylamine.

Typical problems experienced when using unsilanised fillers including silica flour and aluminium trihydrate include water absorption and ponding or film formation on high voltage insulators, and water ingress leading to a breakdown of the epoxy silica structure and loss of dielectric properties.

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Hydrophobicity is a desirable property for high voltage insulators for a number of reasons, including the ability to inhibit water ingress and penetration into the silica-epoxy matrix. Performance and durability can be improved as the epoxy is less susceptible to hydrolysis and polymer breakdown (which leads to eventual failure in strength and electrical properties).

10

Some degree of improved hydrophobicity and reduced water ingress into the polymer matrix is possible using standard epoxy-silane treated silica due to the improved cross link density and reduction of voids in the polymer-filler matrix.

15

However, this is not enough to avoid the occurrence of water ponding on the surface of the insulators which can lead to drops in the dielectric constant and dissipation factor.

Epoxy silane treated inorganic flour is used in these systems instead of untreated inorganic flour to also lower the viscosity of resin-filler formulations, improve the processing properties, increase the strength, improve the arc resistance, and improve final electrical performance properties. In contrast to ceramic glaze which can be eroded by windblown sand and dirt, the polymer surfaces are less susceptible to erosion from such abrasive substances.

20

It has been found ultraviolet erosion and weathering of a highly inorganic filled epoxy, EPDM, silicone or other polymer resin filled insulator will eventually expose the surface of the hard underlying inorganic fillers present in the polymer system. Due to the presence of oxidised and degraded polymer, the inherently poor hydrophobicity of the silanol functional inorganic fillers and subsequent, excessive surface roughness, a hydrophilic surface is presented which encourages water

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ponding and deposition of a continuous pollution layer over the surface of the insulator with subsequent poor, long term performance.

5 Excessive ponding can lead to failures described above and encourage contaminants and pollution to accumulate on the surface of an insulator which can create a conductive track that leads to arcing or flash over on the insulator surface.

10 The integrity and performance of the exterior surface of the insulator is a crucial factor in determining the performance of the insulator regarding long term durability, long term hydrophobicity and ultimately long term arc resistance.

For those systems that intend to present long term hydrophobic properties on extended exposure to weathering a greater degree of hydrophobicity is required.

15 Arcing across the face of the insulator can have a serious effect on the insulator performance due to the formation of conductive carbon deposits which may form a permanent conductive path along the surface of the insulator thereby shortening the lifespan of the insulator.

20 Contaminants can be of natural origin, such as salt spray or ocean fog in coastal regions. Industrial sources, agricultural spraying and automotive exhaust can also contribute to eventual reduced water resistance.

25 Compared to silicone, porcelain and EPDM insulators, inorganic filled cycloaliphatic epoxy insulators can offer advantages in cost, weight, tracking, erosion resistance, maintenance requirements, flash over and corona resistance, design versatility and manufacturing complexity. However, such insulators have demonstrated inconsistent performance particularly when hydrophobicity of the insulator is lost on exposure to atmospheric conditions. Deposition of fillers and a
30 continuous water sheet leads to arcing occurring across the face of the insulator.

The infusion of a strong dipole such as water will adversely affect the dielectric properties of inorganic-filled epoxy high voltage insulating products in particular. The dielectric constant and dissipation factor are particularly susceptible in these systems and a leakage current can be formed through the inorganic-polymer matrix that will eventually rise to unacceptable levels.

A low viscosity cycloaliphatic epoxy-anhydride system with a well silanised silica filler can enable a higher silica content and a subsequently cheaper system wherein the expensive epoxy and anhydride resins are replaced by silica while retaining other physical, electrical and durability properties such as mould shrinkage, tensile, flexural and compressive strength, dielectric constant, moisture resistance, cure properties and exterior durability.

A significant contribution to cost and other properties is possible in an epoxy inorganic insulator when modifications are made to the filler due to a high loading of inorganic filler of over 64% in the final cured product.

Additionally, a lower viscosity product will give a faster cycle time due to reduced mould filling time and can give reduced costs in processing especially where multi cavity tooling is used.

Due to a faster cycle time an increase in reactivity with a faster time to polymerise is possible by increasing the catalyst level and therefore achieving less time spent in the mould overall. Catalyst loadings and gel time specifications are commonly adjusted taking into account the time it takes to fill a mould completely while avoiding premature gelation in the runners and gates.

US Patent No. 4,141,751 discloses the modification of various fillers with a variety of organo-functional silane coupling agents to produce various polymer compositions.

US Patent No. 3,227,675 describes the surface treatment of kaolin clay with up to 10% by weight of an organo-functional silane to improve reinforcing properties in thermosetting resins .

5 As disclosed in US. Patent No. 4,189,392, erosion inhibiting properties can be imparted to a filled, polymeric insulating material by the addition of a hydrophobic, fluorine substituted, non ionic compound. Hydrophobic properties are improved by the addition of the hydrophobic additive. However, the primary intention is to slow the potential for water ingress and subsequent erosion, not to give
10 the surface hydrophobic properties and improve water beading. Hydrophobic pre-treatment of the filler before addition of the filler to the system is briefly mentioned. However, the primary recommendation is the post-addition of the fluorine-substituted hydrophobic additive. Mineral fillers can often be a critical factor in the processing of epoxy or polyester polymeric composites in particular mainly due to
15 the high loadings that are typically used such as 100-180 phr or higher.

Stable condensation products are formed with inorganic, aluminium, zirconium, tin, titanium, and nickel. Less stable bonds are formed with oxides of boron, tin and carbon. Alkali metal oxides and carbonate do not form bonds with the silanol groups.

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US Patent Nos. 2,665,264, 2,744,879, 2,831,828, 2,831,829, and 2,897,173 disclose that certain natural and synthetic silica fillers and metal silicate fillers respond well to organosilane coupling agents. However, natural and synthetic calcium carbonates and other non-siliceous mineral fillers do not show any
25 significant or useful response mainly due to the absence of suitable hydroxyl groups on the surface of the fillers for bonding with alkoxysilyl groups on the silane.

US Patent No. 6,420,456 discloses a two stage process whereby various hydrophilic fillers are hydrophobicized first by treatment with an amino silane,
30 followed by treatment with an alkyl or fluoro silane with hydrophobic properties to produce fillers for use as fillers in polymer master batches including compounds of rubber.

Japanese Patent No. 59-81650 discloses that the improvement in the hydrophobicity and triboelectric charge of a fine silica filler is insufficient when the number of carbon atoms for the treatment chemical bonded to each silicon atom is 8.

5 As the number of carbon atoms in the substituent groups bonded to each silicon atom is increased, the steric hindrance thereof becomes so large that silanol groups at the surface of the silica filler, which exist at small intervals of 5 to 6. Angstrom cannot be entirely treated. However, it is recognised a large substituent group is desirable as it is efficient in reducing the presence of water molecules near
10 the silicon atoms. It has been discovered it is difficult to treat all silanol groups with a treatment agent containing large substituent groups however when a treatment agent with small substituent groups is used almost all of the silanol groups at the surface of the silica fillers are treated. This patent further discloses that efficient treatment can be accomplished by first treating the silica fillers with a large-
15 substituent silane coupling agent and then treating the silica with a small-substituent silane coupling agent that will fill the spaces on the silica between the long chain large substituent silanes.

 A mixed silane system is described in US Patent No. 4,436,847, which
20 describes increasing the efficiency of silane coupling agents, particularly mercaptosilane coupling agents as used in the tyre industry, by using an alkoxy silane in combination with the mercaptosilane to form a coupling composition. The improvement in hydrophobicity enables a stronger filler however it is our contention the use of three distinct silane species including mildly hydrophobic, strongly
25 hydrophobic and an organo-functional species will give enable a greater performance to be achieved.

 US Patent No. 3,567,680, US Patent No. 4,455,343, and US Patent
30 No. 6,770,327 disclose the use of a plurality of silanes including aminoalkylalkoxy, mercaptosilane and silanes comprising, alkyl or hydroxyalkyl-functionalized siloxanes for the treatment of filler in order to achieve higher filler reinforcement of

elastomers, plastics and coatings and introduce hydrophobic properties to glass fibre strands for thermoplastics.

US Patent No. 4,072,796 discloses a process where a precipitated silica is
5 treated with a prepolycondensed organohalosilane or a prepolycondensed mixture of organohalosilanes. The hydrophobically treated precipitated silica is filtered, washed, dried, and tempered at about 300°C to 400°C.

US Patent No. 6,841,197 discloses oligomer mixtures of n-propylethoxy
10 silanes, and their use as treatments for fillers for use as reinforcing agents, surface modifying agents, or in coatings.

US Patent No. 6,455,158 relates to the silanization or surface treatment of
minerals with alkylsilanes and alkylsilane copolymers and to alkylsilane copolymers
15 useful for surface treating fillers. The alkylsilane copolymers comprise at least two different monomers and find utility for the surface treatment of white fillers, such as titanium dioxide, for improving the dispersability and processability of the filler when compounded with a polymeric material such as polyolefins.

EP 0 518 057 discloses mixtures of vinyl-/alkyl-/alkoxy-containing
20 siloxanes, used as crosslinking agents for thermoplastic polyolefins.

Mixtures of aminopropyl-/alkoxy-/alkyl-functional siloxane oligomers are
disclosed in German Patent Application 198 49 308.8, where the mixtures are used as
25 coupling agents in filled thermoplastic compounds, in the coating of glass fibers, or else for silanizing fillers.

However, the concept of using a dual silane blend incorporating functional
and non-functional types is not disclosed nor is the use of a plural blend that
30 contributes both hydrophobicity and functional groups as a treatment system.

US Patent No. 4,141,751, US Patent No. 4,151,154, and US Patent No. 4,344,799 disclose the treatment of colloidal silica and pyrogenic silica, produced by pyrolysing a silane compound. US Patent No. 4,151,154 discloses a process for the treatment of inorganic fillers with a silane that possesses a
5 polyalkylene oxide to give fillers with enhanced performance in fillers and/or filled paints and plastics, and in reinforcing plastic composite structures.

This process of producing synthetic silica by pyrolysis ensures the production of a consistent filler composition within tight specifications that allows
10 for a precise, reliable treatment system. This invention enables the treatment of mined minerals that require flexibility in formulating and adjusting treatment systems due to the potential variability in composition.

US Patent No. 6,455,158, US Patent Application 2005/0129602 A1,
15 US Patent 7,238,387, US Patent 7,255,735, and US Patent No. 3,227,675, disclose the treatment of various minerals with non-functional alkylsilanes and alkylsilane copolymers in order to improve the dispersability and processability when compounded with various fillers, oils and polymeric materials for various applications including filled polymeric systems, sunscreen and toner filler for image
20 forming processes. US Patent No. 6,455,158 discloses the process for the silanization or surface treatment of various minerals with non-functional alkylsilanes and alkylsilane copolymers to improve the dispersability and processability when compounded with a polymeric material such as polyolefins.

25 US Patent No. 4,151,154, US Patent No. 4,141,751, US Patent No. 5,653,794, US Patent No. 5,501,732, US Patent No. 6,214,106, GB Patent Nos. 1,154,835, 785,393, 825,404 and US Patent No. 6,620,234 disclose the treatment of inorganic oxide fillers including silica and titanium dioxide fillers with various non functional aliphatic and cycloaliphatic organosilane and organochlorosilanes in order
30 to introduce hydrophobic properties to improve compatibility and dispersability in various organic paint and solvent systems

US Patent No. 7,250,080 discloses a process for silanization of silica and, surprisingly, discusses the reason for the absence of acid hydrolylates in the treatment process for most other patents to date as being due to the relatively slow rate of silanization when compared to neat 'un-hydrolyzed' treatment.

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It is our belief that to the contrary that the process of silanation at an acid pH may lead to a more efficient coverage due to the formation of silanol monomer. However, the extreme reactivity and the tendency for self condensation and formation of extensive interpenetrating polymer networks on the fillers to be silanated inhibits its use as the end products tend to have an extremely high surface area that is prone to irreversible resin thickening when added to various polymers.

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The post addition of various silicones and siloxanes to silica and other fillers including various clays is known, as is the combination of silane treatment followed by a silicone addition to the functionalised filler.

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US Patent No 621,406 (sic) discloses the preparation of hydrophobic fillers by treatment with "non-reactive" organic substances, such as dimethylpolysiloxanes which interact with the hydroxyl groups in particular on the surface of the filler either partially or completely through relatively weak Van Der Waals forces and/or electrostatic interactions. Due to the relatively weak interaction of the dimethylpolysiloxanes with the filler surfaces these silicones will diffuse from the fillers on subsequent aging and may be extracted from the fillers during the manufacturing stage. It is not possible to achieve a degree of treatment with covalent bonding on the surface by using large molecular weight silanes or organopolysiloxanes in excess to the available silanol groups present as the excess silane will self condense and not be covalently attached to the surface. For treated silica where some portion has not been covalently attached to a dimethylpolysiloxane, there is a possibility these molecules may have a degree of mobility, which may be detrimental to performance (e.g., in silicone rubber applications for medical purposes or for articles that are safe in food contact, such as

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pacifiers, etc).

US Patent No. 5,607,994, US Patent No. 5,631,310, US Patent No. 5,889,090, and US Patent No. 5,959,004 disclose processes that include the
5 treating of white fillers with at least one silane or a mixture of silanes and at least one polysiloxane resulting in improved processability and performance in thermoplastics. Preferred silanes are alkyl trialkoxysilanes. These patents also disclose processes for treating white filler with at least one non-functional silane or a mixture of silanes with at least one polysiloxane resulting in improved processability in thermoplastics
10 compounding and improved performance properties, such as lacing resistance, in a polymeric matrix.

US Patent No. 3,027,896, US Patent No. 5,607,994, US Patent No. 5,631,310, US Patent No. 5,889,090, and US Patent No. 5,959,004 each disclose
15 processes for treating various white fillers and oxide fillers with an alkyl silane or mixture of silanes and at least one dimethylpolysiloxane oil to give hydrophobic properties..

DE 26 28 975 and DE 27 29 244 describe preparing hydrophobic silicas by
20 reacting a precipitated silica with silicone oil or dimethyldichlorosilane, respectively. The silane and silicone oil are added in reverse order for both cases. However, the hydrophobicizing step for both is followed by heat treatment at between 200°C and 400°C.

25 US Patent No. 3,027,896 discloses a method for treating an inorganic oxide filler with a mixed solution comprising an dimethylpolysiloxane and a silane compound in order to improve reinforcement of polar resins. It has been found the use of standard linear dimethyl polysiloxane types which are readily available at competitive prices impart a greater degree of hydrophobicity to fillers than the cyclic
30 organo-polysiloxane which is believed to be preferable in accordance with prior arts.

Silicone oils used may include reactive silicone oils such as amino-modified silicone oil, epoxy-modified silicone oil, carboxyl-modified silicone oil, carbinol-modified silicone oil, methacryl-modified silicone oil, mercapto-modified silicone oil, phenol-modified silicone oil and heterofunctional group-modified silicone oil.

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Non-reactive silicone oils may be used in place of a reactive silicone oil or as an addition to a reactive oil and include polyether-modified silicone oil, methyl styryl-modified silicone oil, alkyl-modified silicone oil, fatty acid-modified silicone oil, alkoxyl-modified silicone oil and fluorine-modified silicone oil; and straight
10 silicone oils such as dimethylsilicone oil, methylphenylsilicone oil, diphenylsilicone oil and methylhydrogensilicone oil. An alkyl or fluoroalkyl modified silicone oil is preferred and these include dimethylsilicone oil, methylphenylsilicone oil, methylhydrogensilicone oil and fluorine-modified silicone oil. These silicone oils may preferably have a viscosity at 25°C of from 5 to 2,000 mm², more preferably
15 from 10 to 1,000 mm², and still more preferably from 30 to 100 mm².

If the viscosity is less than 5 mm², no sufficient hydrophobicity can be obtained in some cases. If it exceeds 2,000 mm², it may become difficult to make uniform treatment when the inorganic fine fillers are treated, or agglomerates tend to
20 be produced and no sufficient fluidity can be obtained in some cases.

DE 26 28 975 discloses that, at a level of just 15% of pyrogenically produced hydrophobic silica in a silicone rubber, the self-levelling properties of the silica disappear and that, at 20%, flowable compounds are no longer obtained.
25 However, all of the mechanical properties are improved. This patent teaches that it is therefore desirable to have pyrogenically produced hydrophobic silica that is able to be used at high loadings, for improving the mechanical properties, but which at the same time still results in flowable final modified compounds.

30 Only a limited amount of hydrophobicizer can be attached covalently to the silica. However, high silane loadings are desired, since they permit decisive improvements in the rheological properties, such as the thickening. It has been found

that relatively low silane contents of less than 3.1% lead to pyrogenically produced hydrophobic silicas which have a strong thickening action in silicone rubber formulations.

5 German Patent No. 198 18 924.9 describes a process for treating fillers with an organosiloxane composition, where, besides OH groups, the organosiloxane has at least one amino-functional group and, if desired, other functional groups selected from the group consisting of alkyl, haloalkyl, alkenyl, glycidyl ether alkyl, acryloxyalkyl and methacryloxyalkyl. Fillers of this type are used in adhesives,
10 sealing compounds, polymer compounds, paints and surface coatings.

 US Patent No. 5,035,748, US Patent No. 4,810,305, US Patent No. 5,035,748, US Patent No. 5,116,886 , US Patent No. 5,908,660, US Patent Nos. 7,186,440, 7,220,449, and 7,250,080 describe processes for treatment of various
15 inorganic fillers with one or more polyorganosiloxanes, siloxane gels, colloidal silica and silicone oils to introduce hydrophobic properties.

 US Patent No. 5,009,874, discloses a method for making a hydrophobic, precipitated silica, useful as a reinforcing filler in silicone elastomers whereby the
20 precipitated silica in aqueous suspension is firstly treated with an organosilicon compound then washed with a water immiscible organic solvent to separate hydrophobic silica from the aqueous phase.

 Wax and silicone blends are known in the art and commonly used for polish
25 and mould release and other hydrophobic modifications of products or surfaces.

 US. Patent No 5,154,759 describes a technique for the manufacture of a useful polish produced from an amino functional silicone and a micronised hydrophobic amide functional wax. However, its application as an internal or
30 external mould release agent or its use as a hydrophobic additive into filled polymer systems is not mentioned.

US Patent No 4,476,155 describes a process of producing a moisture cured silicone compound that is able to coat an insulator for exterior use with a more durable hydrophobic coating than that currently available with non reactive silicone oils and greases.

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US Patent Nos 6,939,582 and 7,232,609 describe processes of producing curing silicone compounds with a mixture of non reactive silicone fluid, silica filler, a silane and a condensation catalyst. These are then applied to the surface of an exterior insulator.

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US Patent Nos 4,476,155, 5,369,161 and 5,326,804 describe processes of producing curing silicone compounds with a mixture of aluminium hydroxide, a silane and a condensation catalyst. These are then applied to the surface of an exterior insulator.

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Micronized hydrophobic wax fillers are known in the art as evidenced by US Patent No. 4,846,887 issued Jul. 11, 1989 and are available from Micro Fillers, Incorporated, Tarrytown, N.Y., and are sold under the trademark AQUABEAD.RTM.

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Mould release compositions are commonly applied to articles including heat cured, silica filled, epoxy anhydride systems used for high voltage insulator parts. They can be external release agents whereupon they are applied to the mould either manually or automatically or they may be internal release agents wherein they are added into the filled system in-situ and separate while the polymer is curing in order to migrate to the mould interface and form a low surface tension modified surface to inhibit adhesion of the resin to the mould. Metal moulds are commonly used. However, moulds may be manufactured from other dimensionally and heat stable materials including various plastics and ceramics.

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The use of a mould release compound is imperative where a mould is composed of a complex shape or deep section, is unpolished or poorly polished and the compound used has strongly adhering properties such as an epoxy resin.

5 A variety of mould release agents may be used including silicones, waxes, fluoro-silicones, stearates, oils, fatty acids and other incompatible resins and low surface tension polymers.

Reactive silicone mould release compounds may be applied to a mould and
10 participate in the cure reaction to form a durable silicone composition on the cured finished product that will contribute to long term hydrophobicity.

Examples of reactive silicone oils used for mould release include amino-modified silicone oil, epoxy-modified silicone oil, carboxyl-modified silicone oil,
15 carbinol-modified silicone oil, methacryl-modified silicone oil, mercapto-modified silicone oil, phenol-modified silicone oil and heterofunctional group-modified silicone oil.

JP-A 2-305454 describes epoxy resin mixtures for use in protective coatings
20 having high moisture stability and comprising, besides an epoxy novolak and a phenolic resin, small amounts of a cyclic dimethylsiloxane. Although in these compositions the corrosion caused by the water bound to the surface is substantially prevented, such systems do not achieve a sufficient long term hydrophobic effect.

25 WO 98/32138 describes the use of a reactive silicone oligomer with a terminal glycidyl groups that enable the silicone to become part of a cured epoxy polymer system. The cured product shows improved hydrophobicity and weathering resistance for items such as high voltage insulators however these suffer from a poor self healing effect when exposed to arcing, high cost, inconsistent exterior film
30 thickness for various insulator profiles and eventual loss of hydrophobicity after the surface layer has eventually degraded.

US Patent No. 6,806,311 describes a process whereby a dimethylpolysiloxane mould release agent is blended with an epoxy-functional, reactive silane in order to produce a suitable mould release composition. This is applied to the surface of the mould to give an epoxy resin based article with a silane
5 chemically bonded to the surface to give a durable hydrophobic finish.

Examples of non-reactive silicone oils used for mould release include polyether-modified silicone oil, methyl styryl-modified silicone oil, alkyl-modified silicone oil, fatty acid-modified silicone oil, alkoxy-modified silicone oil and
10 fluorine-modified silicone oil; and straight silicone oils such as dimethylsilicone oil, methylphenylsilicone oil, diphenylsilicone oil and methylhydrogensilicone oil. An alkyl or fluoroalkyl modified silicone oil is preferred and these include dimethylsilicone oil, methylphenylsilicone oil, methylhydrogensilicone oil and fluorine-modified silicone oil.

15

Commonly non reactive hydrophobic dimethylpolysiloxane silicone oils are used as release agents for a variety of filled and unfilled polymer mixes as they are generally heat stable, economical and provide an effective reliable release. Non reactive mould release compounds are commonly used, generally where greater
20 reliability and release from the mould is required.

Due to the abrasive nature of some fillers such as silica when they are used in a filled mix there is poor retention of release agent on the moulded part and subsequently there is a requirement for the mould to be continuously replenished
25 with fresh release agent.

The retention of a hydrophobic dimethylpolysiloxane silicone oil on a moulded part is primarily responsible for early hydrophobicity of a moulded part on exterior exposure however this is generally rapidly depleted and removed by
30 environmental conditions to reveal a resin-rich layer with minimal hydrophobic properties.

It is one of the objects of the present invention to ameliorate these problems by the use of a wax dissolved in a silicone oil that may give more efficient mould release with longer lasting hydrophobic properties.

5 US Patent No 6,491,981 describes a process to permanently modify an insulator surface with organofluorine hydrophobic silane and/or siloxane treatment system. This patent mentions the use of plastic substrates. However, the process will normally require a porcelain, ceramic or other suitable inorganic insulator surface that may enable reaction with the silane. The process is normally conducted by the
10 insulator manufacturer although post application in the field is possible. The use of this process in the field is not as reliable as the application of a silicone grease due to the ability of the grease to encapsulate deposited dust, dirt and other contaminants.

US Patent No 5,437,894 describes a similar invention for general use that
15 employs a similar principle whereby a surface treatment system is used to permanently modify the surface to give hydrophobic properties.

One of the leading causes of product failure in mineral and filler filled polymer systems, such as used in electrical insulators (but not only electrical
20 insulators), is the degradation caused by the infusion and penetration of moisture into the cured filler-polymer matrix. Hydrolysis and breakdown of polymer bonds are common, as is weakening of the total system due to the internal stress caused by the expansion-contraction action of water due to external temperature fluctuations.

25 Organo-functional hydrolysable mixed silane systems containing functional and non-functional silanes have been used in various applications for a number of years mainly for improving the efficient silane deposition on the filler or substrate surface.

30 The use of fillers treated with compatible functional silane surface treatment agents that allow bonding of the fillers to the polymer system improves the strength and impermeability of the system considerably and will slow the rate of moisture

absorbance into the filled polymer. However, unreacted organic functional groups on the silane and other hydrolysable groups on the relevant polymer are susceptible to irreversible chemical breakdown when moisture is present.

5 Commercial silane treatment of inorganic filler in particular has been inhibited in uptake due to fundamental technical difficulties regarding optimum condition for silane activation and deposition on the filler.

10 Organo-functional hydrolysable mixed silane systems containing functional and non-functional silanes have been used in various applications for a number of years with the aim of improving the efficient silane deposition on the filler or substrate surface.

15 The use of a silane for pre-treatment of inorganic substrates and filler surfaces is well documented and a broad range of silanes are offered by a number of silicon producers worldwide for this purpose. Dow Corning alone offers over 90 products.

20 It has been found ultraviolet erosion and weathering of highly filled systems containing hard durable fillers such as silica and/or talc polymers in resins and other plastics such as epoxy, EPDM, urethane, silicone for example may eventually expose the surface of the hard underlying inorganic silica fillers present in the polymer system. Due to the presence of oxidised and degraded polymer, the inherently poor hydrophobicity of the silanol functional fillers and subsequent, excessive surface
25 roughness, a hydrophilic surface is presented which encourages water ponding over the surface and subsequent poor long term performance.

30 Long term exterior hydrophobic properties can be realised when hydrophobic inorganic components are exposed by eventual polymer breakdown on exterior weathering. This can enable a water repellent surface to be produced with a reduced likelihood of water ponding and subsequent product failure due to water ingress.

A silane is a bifunctional chemical and consists of an organic functional or non-functional group at one end of the molecule and hydrolysable inorganic methoxysilyl groups at the other end. Silanes act as molecular bridges between organic and inorganic substances and can give a significant improvement in properties for inorganic filled resin systems in particular.

A large proportion of neutral, unreactive, hydrophobic silane can be advantageous in improving compatibility in the organic or resin rich phase of a polymer matrix as some degree of oleophilicity is experienced with the presence of organic groups on a purely inorganic surface.

The dual nature of silanes enable them to form bonds at the nano level to both an inorganic surface on either a filler or other substrate due to reaction with the methoxysilyl groups and possibly bond to an organic group on another molecule or polymer if the appropriate reactive groups are chosen.

One of the major difficulties in using monomeric epoxy silanes is the poor stability of the epoxy-functionalities due to the tendency of the epoxy-functionalities to exhibit ring opening and premature reaction. Another major difficulty is controlling the hydrolysis and condensation reactions.

Typically, an organosilane such as glycidoxypropyltrimethoxysilane (GPTMS) is used as a treatment for inorganic fillers for use in epoxy resin based products.

GPTMS is a bifunctional organosilane with reactive epoxy groups at one end and hydrolysable inorganic methoxysilyl groups at the other end of the molecule that enable reactions with inorganic hydroxyl groupings on inorganic surfaces due to reaction with the methoxysilyl groups either in a water/alcohol-hydroxylate or with the hydroxyl groups on the surface of inorganic fillers.

Non-functional mildly hydrophobic alkyl silanes are commonly supplied for Filler/pigment treatment and are used to ensure some degree of repellency and controlled interaction between fillers while reducing the tendency for agglomeration, settling and separation when mixed with the polymer system and other
5 filler/pigments. Fillers in paints in particular will commonly experience improvements in gloss, colour development, hiding power, mixing time and final Filler dispersion.

Mildly hydrophobic silanes act to impart mild hydrophobicity and to aid
10 distribution of the cross-linking epoxy-functional silanes throughout the inorganic filler and upon the surface of the inorganic filler. Without the presence of the mildly hydrophobic silanes the cross-linking epoxy-functional silanes are unevenly and inefficiently distributed around the inorganic fillers. Indeed, the cross-linking epoxy-functional silanes may not attach to some inorganic fillers.

15 Attempts to impart hydrophobicity to silica filler using conventional silane treatment methods at a pH range of 3 to 5 have not been successful with locally available silica filler typically supplied at a slightly acidic pH when measured by mixing in a water slurry.

20 For example, the following hydrolysed formulation is provided by silane manufacturers such as Shinetsu: ethanol 70-80%, water 5-10%, GPTMS 1-10%, and acetic acid (to adjust the pH to between 3 and 5) 0.1 to 2%.

25 The hydrosylate so formed is applied to silica filler under vigorous mixing at approximately 10% on the weight of the silica (to give a 0.1 to 1.0% silane loading). The treated silica filler is then dried off at a minimum of 85°C to remove the ethanol, water and methanol by-product from the GPTMS condensation reaction.

30 The resultant treated silica filler was not consistent in structure – hard lumps were detected after drying. If the treated silica filler was broken up and dispersed in the epoxy resin an irreversible reaction occurred whereby the system thickened up to

give a dry mix before one third of the silica filler had been added. It was not possible to process the mixture to produce any epoxy casts at a silica loading of greater than 10%, whereas a 60 to 70% loading normally is comfortably achieved.

5 It is one of the objects of the present invention to ameliorate these problems to produce a lump-free treated filler of a fine, even particle size, with excellent compatibility and low viscosity characteristics compared to an untreated silica when added into a filled polymer system.

10 When a commercially available epoxy silane treated silica is submerged in the bottom of a clear container and water is added to it, the organo-functional silica shows little, if no water resistance properties in that the water will migrate and wet out the silica in a matter of minutes.

15 It is another object of the present invention to ameliorate these problems and produce an organo-functional filler with excellent water resistance properties that will enable it to successfully repel water and afford hydrophobic properties when submerged.

20 It is another object of the present invention to provide a process for hydrophobically treating particles, preferably mineral particles, with a plurality of silanes at an alkaline pH, said plurality of silanes including at least one mildly hydrophobic silane, at least one strongly hydrophobic silane, and at least one cross-linking, functional silane such that a resulting filled polymer shows improved
25 hydrophobic properties on long term exposure when fully cured.

 It is another object of the present invention to provide a process for hydrophobically treating minerals such that a resulting filled polymer containing said treated minerals as filler demonstrates reduced filler settlement and/or resin gelation
30 when stored for extended periods in a highly filled resin system.

It is another object of the present invention to produce a durable internal release agent for a silica filled epoxy-anhydride insulator that will enable reliable release from the mould and give a longer lasting, more durable finish with extended hydrophobic properties. This may also enable a coating or surface treatment to be applied to the article in-situ with no further need or processing of the article after demoulding.

It is another object of the present invention to provide a process for the production of a range of hydrophobic fillers compatible with a broad range of organic polymer systems by the substitution of functional silanes in a plurality of silanes including hydrophobic non-functional alkyl and fluoroalkyl silanes with at least one functional silane that may offer the best possible reactivity and compatibility in a specified polymer system.

It is another object of the present invention to provide early hydrophobic properties to the aforementioned hydrophobically treated minerals for use in filled polymer systems by the addition of (1) a micronised hydrophobic wax, (2) a PTFE wax, (3) a non-functional dimethylpolysiloxane silicone fluid, (4) a dimethylpolysiloxane silicone fluid with functional groups.

It is another object of the present invention to provide a process of imparting hydrophobicity to a silica filled, cycloaliphatic epoxy insulator heat cured with a polyanhydride hardener by the in-situ addition of (1) a plurality of silanes, (2) a hydrophobic wax dispersed in dimethylpolysiloxane silicone oil, (3) a PTFE wax in order to produce an electrical insulator with improved hydrophobic properties and enhanced release from the mould.

It is another object of the present invention to provide a process for improving the performance of a silica filled, cycloaliphatic epoxy voltage insulator, heat cured with a polyanhydride hardener, by the addition of an epoxy-functional, hydrophobically treated silica to produce a system with significantly improved compatibility, reduced viscosity of the procured liquid, improved, and in some

instance exceptional, strength, electrical, exterior performance, improved resistance to water ingress and long term hydrophobic properties.

5 It is another object of the present invention to provide a process of imparting hydrophobicity to a silica filled, cycloaliphatic epoxy insulator, heat cured with a polyanhydride hardener, by the addition of (1) a plurality of silanes and (2) a dimethylpolysiloxane silicone oil to the surface of the mould in order to produce an electrical insulator with improved hydrophobic properties and enhanced release from the mould.

10

Silane treatment of silica has been used to aid compatibility of the silica filler into the rubber elastomer used for tyres. The rubber compound has traditionally been supplied to tyre manufacturers in a mixture comprised of a hydrocarbon rubber elastomer, an oil extender and a fine filler carbon black filler.

15

The hydrophobic nature of carbon black allows for much easier compatibility and dispersion characteristics into the hydrophobic rubber elastomer whereas problems with inherent incompatibility have been experienced with the use of the comparatively hydrophilic silica fillers.

20

Tyres made with formulations incorporating silica show some important advantages over the use of conventional carbon black filler including lower rolling resistance, better traction on the snow and lower noise generation. These characteristics have encouraged the use of silica in tyres and the subsequent development work in the silanising of silica in order to achieve the best performance in rubber elastomer systems.

25

Silane producers have developed a large range of mercapto-functional silanes with a view to supplying suitable technology to aid compatibility in rubber systems.

30

It is another object of the present invention to provide improvements in oleophilicity and hydrophobicity due to the use of a plurality of silanes including a mercapto functional silane, a mildly hydrophobic silane and a strongly hydrophobic silane to further aid compatibility of silica in a rubber elastomer and ultimately
5 improve the long term performance of a mercapto-functional silane treated silica.

The high cost of mercaptoalkyltrialkoxysilanes, the irritating odours associated with the neat materials and the time and energy required to mix them into rubber compositions have inhibited the post-addition of silane into rubber mixtures
10 containing untreated silica, and therefore promoted the pre-treatment of silica.

The amount of silane added is normally between 2 and 10 percent by weight of the silica.

15 US Patent No 3,567,680 discloses use of mercaptosilane grafted inorganic fillers in combination with aminosilane treated filler, to achieve higher filler reinforcement of elastomers and plastics. Suitable silane coupling agents include those described in US Patent No. 4,704,414, and European patent application
0,670,347A1.

20 The use of various organosilane coupling agents such as bis[3-(trimethoxysilyl propyl)]tetrasulfane (Si-168) and mercaptopropyltrimethoxysilane, as a pre-treatment for in silica in the synthetic rubbers has provided equivalent performance to carbon black-reinforced synthetic rubbers for key physical properties
25 such as 300% modulus, tensile strength, abrasion resistance, and heat build-up. Other suitable silanes include bis[2-(triethoxysilyl)ethyl]-tetrasulfane, available under the trade name Silquest RC-2, a mixture of bis[3-(triethoxysilyl)propyl] monosulfane, bis[3-(triethoxysilyl)propyl]disulfane, bis[3-(triethoxysilyl)propyl]trisulfane and bis[3-(triethoxysilyl)propyl]tetrasulfane and higher sulfane
30 homologues- available under the trade names Si-69 (average sulfane 3.5), Silquest(TM) A-1589 or Si-75 (average sulfane 2.0).

Suitable silanes that may be used include the following
:bis[(trimethoxysilyl)propyl] disulfane (Si-166), bis[(triethoxysilyl)propyl]-
disulfane (Si-266), bis[2-(trimethoxysilyl)ethyl]-tetrasulfane, bis[2-
(triethoxysilyl)ethyl]trisulfane, bis[3-(trimethoxysilyl)propyl]disulfane, 3-
5 mercaptopropyltrimethoxysilane, 3-mercaptopropylmethyldi-ethoxysilane, 3-
mercptoethylpropylethoxymethoxysilane, 1,3-bis(3-
acryloxypropyl)tetramethoxydisiloxane, acryloxypropylmethyldimethoxysilane, 3-
methacryloxypropyl-trimethoxysilane, allyltrimethoxysilane, diallyldiethoxysilane,
5-(bicycloheptenyl)triethoxysilane, 5-(bicycloheptenyl)methylmethoxyethoxysilane,
10 isopropoxytriacyltitanate, diisopropyl dimethacryltitanate, diethoxydi(3-
mercaptopropoxy)zirconate, triisopropoxy-(2-mercptoethoxy)zirconate, and
di[neopentyl(diallyl)oxy]-di(3-mercaptopropoxy)-zirconate.

15 SUMMARY OF ASPECTS OF THE INVENTION

The present invention outlines a process for achieving the conditions for optimum deposition of the silane treatment onto a filler.

20 We have found a combination of mildly hydrophobic and strongly hydrophobic silanes results in efficient entanglement of the alkyl groups on the silanes.

25 According to one aspect of the present invention there is provided a process for imparting hydrophobicity to particles, preferably mineral particles, said process including the step of mixing said particles with a blend of a plurality of silanes at an alkaline pH.

30 Throughout this specification and the claims that follow, the term "blend" is to be understood to encompass homogeneous and heterogeneous mixtures and emulsions.

The said blend of a plurality of silanes includes at least one mildly hydrophobic silane, at least one strongly hydrophobic silane, and at least one organo-functional silane.

5 The group of mildly hydrophobic silanes includes alkyl silanes with a carbon chain length of up to and including six carbon atoms either in a linear, cyclised, aromatic or branched structure, not excluding organo-functional modified ??????. These may be present on the same structure with functional groups such as epoxy, amino, diamino, vinyl, acrylic, mercapto and isocyanato groups. These may
10 also be present as a cyclised structure including chlorophenyl, bromophenyl and phenoxyphenyl groups.

Examples of mildly hydrophobic silanes include alkylsilanes, such as methyltrichlorosilane, methyltrimethoxysilane, methyltriethoxysilane, n-
15 propyltriethoxysilane, hexamethyldisilazane, trimethylsilane, trimethylchlorosilane, trimethylethoxysilane, dimethyldichlorosilane, methyltrichlorosilane.

The group of strongly hydrophobic silanes includes alkyl and fluoroalkyl silanes with a carbon chain length greater than three and up to and including twelve
20 carbon atoms either in a linear, cyclised, aromatic or branched structure. These may be present on the same structure with functional groups such as epoxy, amino, diamino, vinyl, acrylic, mercapto and isocyanato groups. These may also be present as a cyclised structure including chlorophenyl, bromophenyl and phenoxyphenyl groups.

25 The strongly hydrophobic silanes contain long organophilic/polymer-compatible alkyl chains which extend out further from the inorganic fillers into the polymer than the shorter alkyl, mildly hydrophobic chains when the treated inorganic filler is mixed into the polymer system and enable improved organic polymer compatibility of the treated surface.

30

The bulky alkyl groups attached to the silica fillers by the reaction with the strongly hydrophobic silanes serve to sterically limit the interaction of water

molecules with the surface and therefore serve to 'shield' organo-functional groups such as epoxy groups from potential hydrolytic breakdown.

These strongly hydrophobic silanes include long chain alkyl silanes, i.e.,
5 (C3-C12alkyl) tri alkoxy silanes, and fluorosilanes and include propyl
trimethoxysilane, propyl triethoxysilane, octyl trimethoxysilane, octyl triethoxysilane
and fluoroalkylsilanes, isopropyltrimethoxysilane, octyltrichlorosilane,
isooctyltrimethoxysilane, hexadecyltrimethoxysilane, octadecyltrichlorosilane,
cycloalkylsilanes, such as cyclohexyltrimethoxysilane, cyclopentyltri-chlorosilane,
10 and cyclohexyltriethoxysilane, cycloalkenylsilanes, such as cyclohexenylethyl-
triethoxysilane, cyclododecadienyltrichlorosilane, cyclooctenyltrimethoxysilane, and
also tetraethoxysilane.

The at least one strongly hydrophobic silane may be selected from the group
15 consisting of an ethoxy or propoxy silane with a slower rate of hydrolysis and
subsequent silanol formation than the organo-functional and mildly hydrophobic
silanes respectively.

The silanes can be hydrolyzed and/or condensed prior to contact with a
20 mineral filler as the presence of water as a diluent will cause hydrolysis and/or
condensation of the silanes through the hydrolyzable groups on the silanes.

The at least one organo-functional reactive silane is selected from the group
consisting of epoxy silanes, aminosilanes, isocyanatosilanes, methacryl silanes,
25 mercaptosilanes and vinylsilanes, not excluding alkyl, phenyl or fluoroalkyl modified
moieties.

The silane compounds may include alkoxy silanes such as methoxysilane,
ethoxysilane and propoxysilane. Alteration of the alkoxy group enables
30 modifications of the reaction threshold and the speed of reaction.

The organo-functional, or organo-nonfunctional groups may include alkyl, epoxy, amino, etc., at the end of a long or short, linear or cyclised alkyl chain, e.g., glycido (C3-C8) alkyl. The other end of the silane molecule, which reacts with inorganic hydroxyl groups is an alkoxy group which can be short chain (such as methoxy) or longer chain such as ethoxy.

Suitable silanes may include halosilanes such as chlorosilane, bromosilane and iodasilane. Other silanes may include silazanes, hydrosilanes, alkylsilanes, arylsilanes, vinylsilanes, acrylsilanes, epoxysilanes, silyl compounds, siloxanes, silylureas, and silylacetamides.

Any of these silane compounds may be used in plurality.

The manufacture of a hydrosylate with subsequent activation of silanol groups may not be necessary as hydrolysis and/or condensation may also occur due to the presence of atmospheric moisture and/or water molecules normally found on the surface of the mineral filler.

Silane treatment of fillers occurs for similar reasons to substrate treatment and includes the ability to modify the surfaces of individual fillers, fillers and fillers with the same functional and non-functional groups. The specific use of a silane blend including three distinct silane species including mildly hydrophobic, strongly hydrophobic and an organo-functional species as outlined in the present invention is not disclosed in prior art documents such as US 3,567,680, 4,455,343 and 6,770,327.

The ratio of silanes to filler is generally between 0.5 and 2.0% by weight. However, due to the varying low and higher molecular weights of the various silanes and subsequent dimers and oligomers formed the density of silane deposition around a silica filler can vary, indeed a build-up of silane may occur due to self condensation. Additionally, inorganic filler size and surface profile vary. A batch of inorganic filler with a large amount of "fines" will have a greater surface area and "silane demand" than a coarser inorganic filler batch.

Advantages of filler modification include greater compatibility of the filler into the organic polymer system it is dispersed into. The deposition of appropriate functional groups can enable reactivity with functional groups on the polymer used and lower surface tension differences between the inorganic filler surface and polymer to improve penetration and wetting out of the filler and achieve a tighter cross link matrix with minimal voids or air gaps between the filler and cured polymer.

Increased compatibility improves the rheological and flow properties of the system ensuring better flow and substrate wetting properties. The greater compatibility enables a higher loading of filler to be achieved while retaining the original 'un-treated' viscosity with no sacrifice in porosity that will normally occur due to voids in a finish caused by inefficient wetting of the polymer.

The benefits of greater flow in paints can include a lower requirement for solvent and enable a higher solids system, while in plastics improved flow can lead to less pressure required to pump products including lower pressure for the mould injection process.

In silicone rubber formulations high silane deposition on the silica is desired, since IT permits decisive improvements in the rheological properties, such as the thickening, i.e., low yield point and low viscosity, of the compounds.

As a measure of the thickening, it is possible to utilize the Dibutyl phthalate (DBP) number. The DBP number indicates the absorption capacity of a silica for DBP oil. The measurement technique shows the amount of Dibutyl phthalate, in grams, on a sample of 100 grams, at which a dry mix is observed with a significant increase in force in mixing the compound.

Minor variations in filler properties can cause significant variations in the viscosity of the finished product. Generally a low viscosity contribution is desirable

in fillers as it can enable higher loadings to be achieved before undesirable thickening occurs.

5 The hydroxyl groups on the surface of minerals are usually hydrophilic and incompatible with polymers however these hydroxyl moieties enable reactions with a number of silanes. Inorganic filler is mostly dry (98%+) but fillers need not be completely dry as the adsorbed water on the surface helps the reaction with further hydrolysis due to further water exposure forming more silane-silane bonds, strengthening the system.

10

Other fillers that may be treated to give hydrophobic properties for use in filled polymer systems include metal fillers, glass fillers, glass beads, semimetal oxides and metal oxides, typically SiO₂ (aerosol, quartz, quartz filler, synthetic silica flour), aluminium oxide and titanium oxide, metal hydroxides, such as Mg(OH)₂,
15 Al(OH)₃ and AlO(OH), semimetal nitrides and metal nitrides, for example silicon nitride, boron nitride and aluminium nitride, semimetal carbides and metal carbides (SiC), metal carbonates (dolomite, chalk, CaCO₃), metal sulphates (baryte, gypsum), mineral fillers and natural or synthetic minerals, mainly from the series, for example zeolite (in particular molecular sieves), talcum, mica, kaolin, wollastonite, bentonite
20 and others.

A higher loading of filler in a system can give various benefits which are dependant on the filler used such as greater opacity with inorganic coloured fillers, greater strength, less shrinkage, improved chemical resistance with the harder fillers
25 such as the silicas or better impact resistance with softer fillers such as talc. Generally greater cost savings on a weight basis where a cheaper filler is used to replace an expensive resin component are possible.

Different coloured, shaped, sized, structured and chemically different fillers
30 are able to form more homogenous systems with silane and other filler pre-treatment systems that enable controlled interaction between the individual fillers, polymer, plasticiser, solvent, gelatinous clay, cellulosic and modified inorganic-based

thickeners, and other additives including silicone oils and surfactants in both the dry and the liquid phases.

The interpenetrating net work theory is commonly used to describe the
5 mechanism of coupling of the inorganic and organic /polymer surfaces. The theory contends that the silane will first bond to the substrate or filler surface and then self polymerise with other silane molecules to form a high surface area, three dimensional siloxane network of around 10-20 molecular 'chemisorbed' layers that the polymer can diffuse into and entangle with. A loose 'open' alkoxy siloxane
10 network is preferred due to the greater polymer chain interpenetration and entanglement possible.

Amongst the siloxane network are many functional groups that enable reaction of the polymer. The concept may almost be viewed as creating a porous
15 surface in which the polymer may 'soak' into. It may be that an excessive degree of porosity is undesirable due to the effect on physical thickening caused by the increase in surface area.

There can be a significant amount of 'physisorbed' silane on top of the
20 chemisorbed layer that is not reacted with it and is up to 200 layers thick.

A condensed siloxane layer can be produced on the surface of a filler from a reactive silane and may present more reactive sites than the functional groups of the reactive polymer can consume. Unreacted functional groups such as epoxy groups
25 from an epoxy silane on the filler can remain as potential points for hydrophilic attack.

The silane may be added into the polymer system in-situ as a reactive component and offer both organic cross linking with the functional group on the
30 silane as well as offering the final polymer an opportunity to chemically bond with the inorganic surface.

Silanes can offer invisible, hydrophobic and oleophobic treatment of substrates by depositing hydrophobic, non-functional alkyl and highly hydrophobic/oleophobic non-functional fluoroalkyl groups. This can enable relatively porous substrates like concrete to attain a significant measure of hydrophobicity and water repellency without any visible difference to the appearance. A strongly oleophobic fluoroalkyl treatment can enable a surface to attain a certain measure of resistance to graffiti.

The present invention is believed to result in a greater hydrophobic efficiency and less possibility for water ingress due to stated, specific surface treatment of the individual filler fillers before incorporation into the polymer. The major improvement of both hydrophobicity and strength in the invention is due to separate pre-treatment of the inorganic filler with the specified blend of silanes that include a polymer-compatible organo-functional silane, a mildly hydrophobic silane and a strongly hydrophobic silane which may be fluorinated.

The appropriate silanes to be used for any system are primarily dependant on the silane/polymer reactivity however other factors including surface energy, wet out, absorption, adsorption, acid-base interaction, interpenetrating network formation, and covalent reaction must be considered. It is also our belief that silica may be treated once with a plurality of silanes in order to achieve the desired hydrophobic effect and a stabilised triboelectric charge when used in the electrographic industry.

A pre-hydrolyzed and condensed silane can be produced to control the degree of condensation and final composition of the hydrolyzed moieties. An oligomeric structure can be produced with controlled molecular weight, good film formation and dispersion properties because the silane terminations are already partially or totally condensed.

30

The process of self condensation can continue to produce higher molecular weight oligomers and eventually large siloxane networks. Condensation can occur

parallel to hydrolysis once a certain amount of silanol groups have been formed. The competing reactions of self condensation and reaction with the hydroxyl groups on the surface of the filler will be influenced by varying conditions including pH, concentration of the silane in the hydrosylate, solvent type in the hydrosylate,
5 temperature, catalyst, substrate composition and silane type.

The slowest rate of hydrolysis of alkoxy silanes occurs at a neutral pH in aqueous environments while the effect is accelerated in both acid and basic conditions.

10

Silane treatments in the prior art patents referred to in this specification commonly consists of the direct post addition of unhydrolysed silane into a filled polymer system for a number of reasons including convenience, speed, and minimizing possible mistakes in production due to the introduction of a separate
15 process.

A hydrosylate is used in order to 'activate' and produce reactive silanol-functional groups on the silane that may react with -OH groups on the surface of the inorganic filler or on other inorganic substrates. The silanol functionality on
20 individual silane species also enables a reaction between the silanes to produce dimeric, oligomeric and possibly polymeric siloxanes.

Hydrolysis of the methoxy moieties of a silane generate methanol and form silanol groups, which in a subsequent self-condensation reaction can form dimeric
25 and oligomeric structures with the liberation of methanol. These may further condense in a water-alcohol hydrosylate media to form polymeric structures. Monomeric, oligomeric or polymeric silanols can then react with the surface hydroxyl groups present on inorganic surfaces to form very stable three dimensional siloxane networks.

30

Suitable solvents that act as a medium for the hydrosylate include primary alcohols such as methanol, ethanol and secondary and tertiary alcohols, including n-

propanol, i-propanol, i-butanol, amyl alcohol, hexyl alcohol, n-octanol, i-octanol, ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol as well as mixtures of these alcohols with aromatic, aliphatic or cycloaliphatic hydrocarbons, such as toluene, cyclohexane, hexane, octane, or open-chain or cyclic ethers such as diethyl ether, dibutyl ether, tetrahydrofuran, 1,3-dioxolane and their mixtures with alcohols or amides, such as dimethylformamide and dimethylacetamide.

In acidic aqueous environments hydrolysis is initiated by attack of a proton on the electronegative oxygen component of the alkoxy group. The protonated alkoxide is then released as the corresponding alcohol in exchange for water. The last step is regeneration of the proton.

In basic aqueous environments hydrolysis is initiated by attack of the hydroxide ion on the electropositive silicon atom. The alkoxide anion is subsequently released followed by abstraction of a proton to form the corresponding alcohol with the regeneration of the hydroxide anion.

The atom of the alkoxy silane which is attacked changes as the pH of the environment changes. However, it has been discovered that an alkaline hydrosylate with the subsequent production of silanol functional dimeric and oligomeric groups from self condensation of the silane is required to give a more reliable, consistent and superior quality in the finished product.

It has been observed that due to the inherent acidity of the locally available inorganic filler a premature, uncontrolled reaction occurred when attempting to treat the inorganic filler with a neutral or slightly acidified epoxy silane hydrosylate.

A pH in the range 3-5 is specified by silane suppliers such as Shinetsu (Japan) to minimize the formation of high molecular weight oligomers resulting from the silane reacting with itself. The low pH is also claimed to improve the hydrolysis rate.

According to Shinetsu technical literature the greatest percentage of monomers (80%) and the lowest percentage of oligomers (0%) occur at around pH 3-5 while dimer concentration sits at around 20%.

5

Shinetsu also state that at a slightly alkaline pH around 7-8 there are around 10 % oligomers, 40% dimers and 50% monomers for a silane such as GPTMS (glycidoxypropyltrimethoxysilane).

10

A 50 % GPTMS concentration gives almost 100 % molar ratio of oligomers. At a 5% GPTMS concentration the ratio is oligomers (50%), dimers (40%) and monomers (10%). A 90 % GPTMS concentration has 10% oligomers, 30% monomers and 50% dimers.

15

Specific claims for the inclusion of an organo-functional silane as part of a hydrophobic silane composition have not been made in the prior art. The present invention, in contrast to GB 1303432, proposes a plural system whereby silanes containing organic functional groups are used in conjunction with hydrophobic, non functional silanes.

20

The said particles may be fillers including at least one material selected from the group consisting of semimetal oxides and metal oxides, silica (aerosil, quartz, quartz filler, synthetic silica flour), oxides of zinc, titanium, aluminium, silicon, zirconium, lead, chromium and iron, aluminium trihydrate, semimetal nitrides and metal nitrides (for example, silicon nitride, boron nitride and aluminium nitride), semimetal carbides and metal carbides (for example, SiC), metal carbonates (for example, dolomite, chalk, CaCO₃), calcined clay, delaminated kaolin clay, metal sulphates (baryte, gypsum), non-mineral fillers, including carbon black, mineral fillers and natural or synthetic minerals, including from zeolite (in particular
25
30
molecular sieves), talcum, mica, kaolin, wollastonite, bentonite, metal filler, glass filler, glass beads and others.

According to another aspect of the present invention there is provided process for imparting hydrophobicity to various fillers of inorganic filler (including non-mineral material such as carbon black) with a blend of a plurality of silanes, said process including admixing at least one mildly hydrophobic silane, at least one
5 strongly hydrophobic silane, and at least one organo-functional silane with said fillers under controlled alkaline conditions.

According to another aspect of the present invention there is provided a process for imparting hydrophobicity to said fillers, said process including the steps
10 of admixing a slurry containing said fillers with a blend of a plurality of silanes under controlled alkaline pH in a mixing vessel, and subsequently drying the treated fillers.

According to another aspect of the present invention there is provided a process for treatment of inorganic fillers including the deposition of both organo-
15 functional and hydrophobic groups on the surface of the fillers by a blend of a plurality of silanes, their hydrosylates or resulting condensates. In some instances the manufacture of a hydrosylate with subsequent activation of silanol groups may not be necessary as hydrolysis and/or condensation may also occur due to the presence of atmospheric moisture and/or water molecules normally found on the surface of the
20 mineral filler.

Suitable solvents that act as a medium for the hydrosylate include primary alcohols such as methanol, ethanol and secondary and tertiary alcohols, including n-propanol, i-propanol, i-butanol, amyl alcohol, hexyl alcohol, n-octanol, i-octanol,
25 ethylene glycol, 1,2- and 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol as well as mixtures of these alcohols with aromatic, aliphatic or cycloaliphatic hydrocarbons, such as toluene, cyclohexane, hexane, octane, or open-chain or cyclic ethers such as diethyl ether, dibutyl ether, tetrahydrofuran, 1,3-dioxolane and their mixtures with alcohols or amides, such as dimethylformamide and
30 dimethylacetamide.

According to another aspect of the present invention there is provided a process for imparting hydrophobicity to an inorganic filler, or a plurality of inorganic fillers, wherein a blend of a plurality of silanes is added to the inorganic filler, or a plurality of inorganic fillers, in the form of an alkaline hydrosylate in a mixing vessel
5 and subsequently the treated filler or fillers is/are dried.

According to another aspect of the present invention there is provided process for imparting hydrophobicity to one or more inorganic fillers as hereinbefore disclosed, said method including the step of mixing said fillers with at least one
10 mildly hydrophobic silane, at least one strongly hydrophobic silane, and at least one organo-functional silane, at controlled alkaline pH.

The blend of a plurality of silanes as aforesaid is admixed with a volatile aqueous alcohol blend adjusted to an alkaline pH in the range of 7 to 10 by the
15 addition of a volatile amine to create a hydrolysate prior to the admixing of the hydrosylate with the one or more inorganic fillers.

The alkaline pH adjustment stage of the present invention allows for varying amounts and various types of amines to cater for variations in the acidity of the base
20 minerals to be treated.

The invention allows for the inclusion and possible adjustment of organo-functional silanes to improve compatibility and subsequent performance properties with various polymers
25

According to another aspect of the present invention there is provided process as aforesaid for the production of a range of hydrophobic fillers compatible with a broad range of organic polymer systems by the selective substitution of organo-functional silanes.
30

Specialised individual silanes are available with a mixture of functional reactive groups and non-functional hydrophobic groups in the same chemical and The group of cross-linking epoxy-functional silanes includes alkyl and fluoroalkyl silanes with a carbon chain length of up to and including twelve carbon atoms either
5 in a linear, cyclised, aromatic or branched structure.

The various silanes listed may also be present as a cyclised structure including chlorophenyl, bromophenyl and phenoxyphenyl groups. They include glycidoalkyl trialkoxysilanes, i.e., glycidoxy (C3-C6 alkyl) tri (C1-C2alkoxy)silanes,
10 glycidoxy propyl trimethoxysilanes and glycidoxy propyl triethoxysilanes, glycidoxy propyl methyl trimethoxysilane, and glycidoxy propyl methyl triethoxysilane.

While the foregoing named glycidoxy propyl trialkoxy silanes and glycidoxy propylmethyl trialkoxy silanes are preferred members of the group of
15 cross-linking epoxy-functional silanes, the group is not restricted to those named.

Most preferred is γ -glycidoxypropyl trimethoxysilane used as an adhesion promoter in epoxy systems. It is a common silane available from most silicone producers including Crompton (A187), Dow Corning (DC6040), Shinetsu
20 (KBM403), Wacker (GF80 and GF82), and Sivento (GLYMO). The Crompton speciality chemicals grade A187 and the Dow Corning product (DC6040) have been used in the process of the invention. However, other manufacturers' versions could be used instead. Using a glycidoalkyl trialkoxysilane with methoxy groups instead of ethoxy groups gives a more reactive silane but the same glycidoalkyl group is
25 deposited.

Organo-functional silanes such as amino or diamino silanes are commonly used in two part epoxy based systems to treat fillers used in polyamine and polamide hardener components and may also contain epoxy reactive or epoxy compatible
30 groups such as amino and diamino groups and these include such types as γ -aminopropyltriethoxysilane.

If the amino or diamino silane is added directly to the polayamine or polyamide hardener component and react with an epoxy group when catalysed the presence of alkoxy groups on the cured polymer will improve the adhesion to difficult substrates such as aluminium or ceramic.

5

Amine functional silanes may also be used as organo-functional groups on non-functional silanes and these may include trimethoxysilyl- γ -propylphenylamine, trimethoxysilyl- γ -propylbenzylamine, trimethoxysilyl- γ -propylpiperidine, trimethoxysilyl- γ -propylmorpholine, and trimethoxysilyl- γ -propylimidazole, 3-aminopropylmethyldiethoxysilane, N-2-(vinylbenzylamino)-ethyl-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxy-silane, trimethoxysilylpropyldiethylenetriamine, N-2-(aminoethyl)-3-aminopropyltris(2-ethylhexoxy)silane, 3-aminopropyl-diisopropylethoxysilane,

10

N-(6-aminoethyl)aminopropyltrimethoxysilane, 4-aminobutyltriethoxysilane, 4-aminobutyldimethylmethoxysilane, triethoxysilylpropyldiethylenetriamine,

3-aminopropyltris(methoxyethoxyethoxy)silane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-2-(aminoethyl)-3-aminopropyltris(2-ethylhexoxy)silane,

3-aminopropyl-diisopropylethoxysilane, N-(6-aminoethyl)aminopropyltrimethoxysilane, 4-aminobutyltriethoxysilane, and (cyclohexylaminomethyl)-methyldiethoxysilane.

Any of these treating agents may be used alone or in the form of a mixture of two or more types, or after their multiple treatment. However, the use of an amino functional silane and an epoxy-functional silane as a blend is not practical due to the reaction between the amino and epoxy groups.

30

Suitable unsaturated organic olefinic silane compounds may be used for unsaturated radical cure systems such as polyester, acrylic and vinyl resin based systems in such industries such as marine, building, aerospace and construction.

5 Suitable silanes include vinyl, allyl, γ -methacryloxypropyl, and the like including vinyltrimethoxysilane, vinyl triethoxysilane, vinyltrichlorosilane, vinyltris(methoxyethoxy)silane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, vinyltris (2-methoxyethoxy) silane, γ -methacryloxypropyltrimethoxysilane, vinyltriacetoxysilane,
10 allyldimethylchlorosilane, allylphenyldichlorosilane, vinyl dimethylacetoxysilane, triorganosilyl acrylate.

Some examples of suitable mercapto functional silanes commonly used for processing rubber in the tyre industry are the following mercapto substituted radicals,
15 such as beta-mercaptoethyl, γ -mercaptoethyl, beta-mercaptoethyltriethoxysilane, Γ -mercaptoethyltriethoxysilane, triorganosilyl mercaptan, trimethylsilyl mercaptan.

Other organo-functional silanes include the isocyanatosilanes used in urethane formulations which are reacted mainly with hydroxylated polymers. these
20 may be used however the present invention utilises specific blends of separate silane entities.

The epoxy-functional silanes are the epoxy-functional types which are the products specified for use in epoxy and epoxy reactive systems. It has been an
25 interesting observation that the present invention enables an epoxy-functional silica to remain stable for over six months at ambient temperature with no sign of settlement or gelation when stored at a loading above 50 parts by weight in a liquid epoxy reactive hardener such as a polyanhydride resin. A comparative conventional epoxy-functional treated silica normally will display hard settlement after a few
30 hours when stored under the same conditions.

It was expected the epoxy-functionality may contribute to a reaction with the carboxyl groups of the polyanhydride hardner. However, good stability with no evidence of resin gelation was not observed after observation over a six month period. It has been speculated that the presence of the bulky long octyl chains beside the epoxy groups on the surface of the filler may inhibit this premature, undesirable
5 reaction between the epoxy and anhydride groups on the hardener.

The amino-functional polysiloxanes are silicone fluids with highly polar pendant aminoalkyl modifying groups that enhance the durability of the film formed
10 by the polysiloxanes present and promotes adhesion of the formed film to the vinyl substrate. Particularly preferred aminofunctional polysiloxanes include reactive and non-reactive hydrolyzable and non-hydrolyzable derivatives which are wholly, or in part, terminally substituted with aminopropyl, aminobutyl, or diamino pendant
chains.

15

It is our belief, in contrast to the teaching of US 6,240,456, that the process of depositing both amino functional and alkyl functional groups on the same filler can be accomplished in the one step by the use of an appropriate silane blend as described herein.

20

Mildly hydrophobic silanes act to impart mild hydrophobicity and to aid distribution of the cross-linking epoxy-functional silanes throughout the inorganic filler and upon the surface of the inorganic filler. Without the presence of the mildly hydrophobic silanes the cross-linking epoxy-functional silanes are unevenly and
25 inefficiently distributed around the inorganic fillers. Indeed, the cross-linking epoxy-functional silanes may not attach to some inorganic fillers

A filler treated with a large proportion of neutral, unreactive, hydrophobic silane will generally demonstrate an improvement in organic phase compatibility
30 with reduced filler agglomeration and settlement when mixed with an organic polymer system.

The requirement for silanes to be used as a surface pre-treatment of an inorganic surface to enable adequate adhesion of subsequent coats is due to the relatively poor adhesion of most organic polymers to ceramic, glass and siliceous surfaces in particular while some will have relatively poor adhesion to metal also and will require the presence of organic groups to both aid their compatibility with the surface and offer the opportunity for some chemical bonding to occur with subsequent coats.

Silane treatments of inorganic surfaces including concrete, ceramic, glass and metal include the ability to offer bonding sites with a number of functional groups, including epoxy, amino, vinyl, acrylic and others. The functional groups are chemically attached by the silane and offer a permanent site for further chemical reactions with organic polymer systems when over-coated as topcoats and primers.

A condensed siloxane layer can be produced on the surface of a filler from a reactive organo-functional silane and may present more reactive sites than the functional groups of the reactive polymer can consume. Unreacted functional groups such as epoxy groups from an epoxy silane on the filler can remain as potential points for hydrophilic attack.

It is our contention that the introduction of hydrophobic properties to the surface of an organo-functional filler can reduce the likelihood of hydrolytic attack and eventual breakdown of unreacted functional groups leading to organo-functional treated fillers with improved durability.

Specialised individual silanes are commercially available with a mixture of functional reactive groups and non-functional hydrophobic groups in the same chemical and these may be used for filler treatment. However, as discussed later, the present invention utilises blends of separate silane entities as the opportunity is afforded for greater formulating flexibility, whereby the individual functional and non functional groups may be substituted in the silane blend in order to optimise

filler properties due to variations in fillers, performance criteria required, cost, varying polymer systems, reaction and manufacturing conditions.

5 The concentration of the at least one organo-functional silane in the hydrophobic silane blend preferably is between 5 and 50% by weight and more preferably between 10 and 30%.

10 The concentration of the at least one strongly hydrophobic silane in the hydrophobic silane blend preferably is between 10 and 80% by weight and more preferably between 50 and 70%.

15 The concentration of the at least one mildly hydrophobic silane in the hydrophobic silane blend preferably is between 5 and 50% by weight and more preferably between 10 and 30%.

The silane hydrosylate is added at a range preferably of between 1 and 50% by weight and more preferably between 3 and 20% by weight on the basis of the filler to be treated.

20 The concentration of silanes in the hydrosylate preferably is between 1 and 50 % by weight and more preferably between 15 and 40%.

25 The concentration of amine used for pH adjustment in the hydrosylate preferably is between 0.0 and 5% by weight and more preferably between 0.1 and 2.0 %.

The concentration of water in the hydrosylate preferably is between 1 and 50% by weight and more preferably between 2 and 10%.

30 The process of the present invention allows for the production of mixed hydrophobic organo-functional silane treated fillers having a high dispersability and low aggregative properties.

The adjustment of the pH between 7 to 10 of the mixed hydrophobic organo-functional silane hydrosylate preferably is by addition of aqueous solutions of primary, secondary and/or tertiary amine compounds such as ammonia and dimethylethanolamine.

5

According to another aspect of the present invention there is provided a process for imparting hydrophobicity to at least one inorganic filler under alkaline conditions wherein the pH is maintained in the range of 7 to 8 by the addition of a volatile amine to a hydrosylate containing a blend of a plurality of silanes prior to the admixing of the hydrosylate with the at least one inorganic filler.

10

According to another aspect of the present invention there is provided a process as aforesaid for imparting hydrophobicity to at least one inorganic filler wherein the total silanes amount is from about 0.1 to about 5.0 weight percent on a dry mineral basis.

15

According to another aspect of the present invention there are provided compositions consisting essentially of at least one hydrophobically treated inorganic filler produced by the foregoing process.

20

According to another aspect of the present invention there are provided resin containing compositions which include hydrophobically treated inorganic flour at a loading of between about 10 to about 90 parts per hundred by weight of resin, and formulations and products, including moulded products, incorporating such compositions.

25

We have found certain waxes to be particularly effective in improving medium to long term hydrophobic properties on exterior exposure for filled polymer systems and these include the micronized filler forms of one or more conventional waxes such as Fischer-Tropsch wax, polyethylene wax, polyethylene-polytetrafluoroethylene wax, polytetrafluoroethylene wax, polypropylene wax,

30

natural wax, mineral wax, montan wax derivatives, fatty acid wax derivatives, amide wax, and mixtures thereof.

5 While the filler size of these micronized wax fillers typically varies from an average diameter of 2-45 microns, filler sizes in the range of 3-12 microns are preferred in the epoxy-silica based formulations in accordance with the present invention.

10 We have found the light stable high melting point waxes such as PTFE particularly effective for retaining hydrophobicity on long term exterior exposure.

Resin-containing compositions containing hydrophobic organo-functional silane treated fillers including silica flour, and optionally wax and/or silicone oil, thereby allowing for polymer cross linking and compatibility while exhibiting
15 exceptional anti-settling behaviour and storage stability when stored in the form of liquid resin systems for use in filled polymer products prior to curing.

According to another aspect of the present invention there is provided processes wherein hydrophobic epoxy-functional silane treated fillers produced
20 according to the aforesaid process, including silica flour and wax and/or silicone oil modified versions, are used in the manufacture of filled polymer products (including high voltage insulators) wherein the filled polymer products contain a post addition of a silane, silicone oil and/or wax component.

25 According to another aspect of the present invention there are provided processes wherein hydrophobic epoxy-functional silane treated fillers produced according to the aforesaid process, including silica flour and wax and/or silicone oil modified versions, are used in the manufacture of filled polymer products (including high voltage insulators). The fully cured products exhibit improved long term
30 hydrophobicity and improved durability due to reduced water ingress into the polymer matrix.

The need for a separate coating step on a production line as envisaged in US 5,437,894 is not required with the invention so proposed due to the in-situ addition of the wax-silicone component into the liquid silica-epoxy mix before moulding.

5 The present invention caters for the use of an external release agent applied to the mould that may enable long lasting hydrophobic properties due to an in-situ reaction with the silica-epoxy matrix on moulding either by a physical diffusion of the wax-silicone components or by chemical crosslinking with available epoxy and/or anhydride groups.

10

The present invention allows a number of advantages over factory coated silicone membrane systems for example including a significantly cheaper product due to the requirement of a coating process to include a further coating step. Other advantages of the present invention include no further raw materials are required, no
15 modifications or additions to the production line, no delays due to the coating process, and no specific mould release considerations.

According to another aspect of the present invention there are provided processes wherein hydrophobic organo-functional treated fillers (including silica) are
20 used in the manufacture of filled polymer products exhibiting improved long term performance (including high voltage insulators) due to the presence of hydrophobic alkyl groups inhibiting potential hydrolysis and breakdown of unreacted hydrophilic functional groups such as epoxy when exposed to prolonged contact with moisture.

25 According to yet another aspect of the present invention there are provided hydrophobic epoxy-functional silane treated fillers, including silica flour and wax and/or silicone oil modified versions, which allow for polymer cross linking and compatibility while exhibiting exceptional anti-settling behaviour and storage stability when stored in liquid resin systems for use in an epoxy or polyanhydride
30 hardener resin systems such as those used in high voltage insulators

The waxes used in the present invention may include the following. e.g., aliphatic hydrocarbon waxes such as low-molecular weight polyethylene, low-molecular weight polypropylene, polyolefin copolymer, polyolefin wax, microcrystalline wax, paraffin wax and Fischer-Tropsh wax; oxides of aliphatic hydrocarbon waxes, such as polyethylene oxide wax; or block copolymers of these; vegetable waxes such as candelilla wax, carnauba wax, japan wax (haze wax) and jojoba wax; animal waxes such as bees wax, lanolin and spermaceti; mineral waxes such as ozokerite, serecin and petrolatum; waxes composed chiefly of a fatty ester, such as montanate wax and castor wax; and those obtained by subjecting part or the whole of a fatty ester to deoxydation, such as deoxidized carnauba was. It may further include saturated straight-chain fatty acids such as palmitic acid, stearic acid, montanic acid and also long-chain alkylcarboxylic acids having a long-chain alkyl group; unsaturated fatty acids such as brassidic acid, eleostearic acid and parinaric acid; saturated alcohols such as stearyl alcohol, eicosyl alcohol, behenyl alcohol, carnaubyl alcohol, ceryl alcohol, melissyl alcohol and also long-chain alkyl alcohols having a long-chain alkyl group; polyhydric alcohols such as sorbitol; fatty acid amides such as linolic acid amide, oleic acid amide and lauric acid amide; saturated fatty bisamides such as methylenebis(stearic acid amide), ethylenebis(capric acid amide), ethylenebis(lauric acid amide) and hexamethylenebis(stearic acid amide); unsaturated fatty acid amides such as ethylenebis(oleic acid amide), hexamethylenebis(oleic acid amide), N,N'-dioleyladipic acid amide and N,N'-dioleylsebasic acid amide; aromatic bisamides such as m-xylenebisstearic acid amide and N,N'-distearylisophthalic acid amide; fatty acid metal salts (those commonly called metal soap) such as calcium stearate, calcium laurate, zinc stearate and magnesium stearate; grafted waxes obtained by grafting vinyl monomers such as styrene and acrylic acid to fatty acid hydrocarbon waxes; partially esterified products of polyhydric alcohols with fatty acids, such as monoglyceride behenate; and methyl esterified products having a hydroxyl group, obtained by hydrogenation of vegetable fats and oils.

30

Also preferably usable are those products obtained by subjecting any of these waxes to press sweating, solvent fractionation, recrystallization, vacuum

distillation, ultracritical gas extraction or molten-liquid crystallization to make their molecular-weight distribution sharp, low-molecular weight solid fatty acids, low-molecular weight solid alcohols, low-molecular weight solid compounds, and other waxes from which impurities have been removed.

5

Micronized wax fillers sold under the trademark AQUABEAD.RTM. products 270E, 418E and 519 are particularly preferred.

10 The process of the present invention allows for production of the aforesaid hydrophobic organo-functional silane treated fillers including silica flour and wax and/or silicone oil modified versions which can achieve the desired hydrophobic effect and stabilised triboelectric charge for use in electrographic copying.

15 The process of the present invention allows for the aforesaid hydrophobic organo-functional silane treated fillers including silica flour and wax and/or silicone oil modified versions to be used as a component of cosmetics to improve flow, feel and softness.

20 The process of the present invention may be used for the production of hydrophobic organo-functional silane treated fillers including silica flour and wax and/or silicone oil modified versions that can be used as a filler in a multitude of materials including, but not limited to elastomers, paints, filled polymer systems including silicone elastomers and epoxy systems for use in voltage insulators, paints, fillers and rubber compounds including tyre treads and shoe soles.

25

According to another aspect of the present invention there is provided a process for imparting hydrophobicity to one or more inorganic fillers, optionally silica, by admixing said one or more inorganic fillers with a plurality of silanes, said plurality of silanes including at least one mildly hydrophobic silane, at least one 30 strongly hydrophobic silane, and at least one mercapto functional silane that allows for polymer cross linking with hydrophobic properties and improved oleophilic compatibility with elastomeric rubber compounds.

The aforesaid hydrophobic, organo-functional silane treated fillers, including silica flour and wax and/or silicone oil modified versions, may be used as a component in the manufacture of tyres, antifoaming preparations or foam regulators in laundry detergents, toners such as those used in photocopiers, and various
5 cosmetic applications.

According to another aspect of the present invention there are provided compositions consisting essentially of the aforesaid hydrophobic organo-functional silane treated fillers including silica flour, and wax and/or silicone oil modified
10 versions at a loading of between 30-70 percent, and formulations and products, including moulded products, incorporating such compositions.

According to yet another aspect of the present invention there is provided a process wherein one or more of the aforesaid hydrophobic organo-functional silane
15 treated fillers (such as silica) is treated by addition of a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight.

According to yet another aspect of the present invention there is provided a process wherein one or more of the aforesaid hydrophobic organo-functional silane
20 treated fillers (such as silica) is treated by the addition of (1) a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight and/or (2) a PTFE wax at a loading of between 0.01-10 parts by weight.

The prior art as discussed does not disclose a process for the
25 dimethylpolysiloxane post treatment of a filler previously treated with a plurality of silanes including at least one mildly hydrophobic silane, at least one strongly hydrophobic silane, and at least one cross-linking organo-functional silane to produce a hydrophobic inorganic filler.

30 It has been discovered a significant impact on the performance of a hydrophobic filler treated with a plurality of silanes including a mildly hydrophobic, a strongly hydrophobic and an organo-functional group can be realised with the post

addition of a polysiloxane and/or wax compound to the silane-treated filler immediately after the silane treatment process.

The present invention is also an improvement of the process disclosed in US 5 6,806,311 whereby the aforesaid hydrophobic, organo-functional silane blend is added to the dimethylpolysiloxane mould release agent to further improve mould release and hydrophobic properties.

The present invention also relates to the addition of an dimethylpolysiloxane 10 silicone oil such as 'Release Agent TN', available from Wacker Silicones (Ger) as described in US Patent 6,294,007 and believed to be composed of an dimethylpolysiloxane containing methyl groups, phenyl ethyl groups, and dodecyl groups bonded to silicon. The aforesaid oil can be added directly to the silica or post added to the filled polymer to improve hydrophobic properties.

15 According to yet another aspect of the present invention there is provided a process wherein one or more of the aforesaid hydrophobic organo-functional silane treated fillers (such as silica) is treated by the addition of (1) a dimethylpolysiloxane silicone oil at a loading of between 0.01-10 parts by weight.

20 According to yet another aspect of the present invention there is provided a process wherein one or more of the aforesaid hydrophobic organo-functional silane treated fillers (such as silica) is treated by the addition of (1) a dimethylpolysiloxane silicone oil at a loading of between 0.01-10 parts by weight and/or (2) a 25 dimethylpolysiloxane silicone oil with functional groups at a loading of between 0.01-10 parts by weight.

According to yet another aspect of the present invention there is provided a process wherein one or more of the aforesaid hydrophobic organo-functional silane 30 treated fillers (such as silica) is treated by the addition of (1) a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight and/or (2) a PTFE wax at a loading of between 0.01-10 parts by weight (3) a dimethylpolysiloxane

silicone oil at a loading of between 0.01-10 parts by weight and/or (4) a dimethylpolysiloxane silicone oil with functional groups at a loading of between 0.01-10 parts by weight.

5 According to yet another aspect of the present invention there is provided a process for the production of a hydrophobic treatment component including melting a hydrophobic wax and/or waxes into a dimethylpolysiloxane silicone oil at a loading of between 0.01-90 parts by weight.

10 According to yet another aspect of the present invention there is provided a process for the production of a hydrophobic treatment component including melting a hydrophobic wax and/or waxes into a dimethylpolysiloxane silicone oil with functional groups at a loading of between 0.01- 90 parts by weight.

15 According to yet another aspect of the present invention there is provided a process for the production of a hydrophobic treatment component including melting a hydrophobic wax and/or waxes into a dimethylpolysiloxane silicone oil at a loading of between 0.01- 90 parts by weight.

20 According to yet another aspect of the present invention there is provided a process for the post-treatment of an untreated or silane pretreated filler with the aforesaid wax and silicone oil composition in order to introduce hydrophobic properties.

25 According to yet another aspect of the present invention there is provided a process for the post-treatment of the aforesaid hydrophobic organo-functional fillers with the aforesaid wax and silicone oil composition in order to improve hydrophobic properties.

30 The present invention is intended to provide a more efficient, reliable method in that the hydrophobic treatment is present at the surface of the article and

throughout the body of the cured matrix. As the surface degrades fresh hydrophobic components are exposed.

The blend of a plurality of silanes on a dry weight basis may comprise from
5 10-40% by weight of mildly hydrophobic silanes, from 40 to 80% by weight of
strongly hydrophobic silanes and from 10 to 30% by weight of cross-linking organo-
functional silanes. Preferably the silane mixture comprises from 15-25% by weight
of methyl trimethoxysilane, from 50 to 70% by weight of octyl trimethoxysilane and
10 from 10 to 30% of an organo-functional silane such as glycidoxypropyl
trimethoxysilane.

More preferably the silane mixture comprises 20% by weight of methyl
trimethoxy silane, 60% of octyl trimethoxysilane and 20% by weight of an organo-
functional silane such as glycidoxypropyl trimethoxysilane.

15

The most preferred mildly hydrophobic silane is methyl triethoxysilane
("MTMS") as it gives a faster reaction and is more suited to a production line where
a high output is required. It was found when trialled the slower reacting silanes such
as glycidoalkyl alkyl diethoxysilanes supplied as glycidoxypropyl methyl
20 diethoxysilane (available as KBE402 from Shinetsu) were too slow for use in the
production line used.

The reaction of MTMS is faster compared to methyl triethoxysilane
("MTES") due to the slower release of the relatively bulky ethanol group on MTES
25 as a by-product of the silane hydrolysis reaction. Both the MTMS and MTES give
the same degree of hydrophobicity as they deposit the same alkyl group (methyl)
onto the inorganic surface.

Some commercially available products include DC6070 from Dow Corning
30 and MTMS from Degussa.

The most preferred strongly hydrophobic silane is octyltriethoxysilane ("OCTEO"). The ethoxy group on OCTEO allows for a slower reaction than the MTMS and GPTMS and allows the octyl group time to form the long octyl chain on the outer surface of an IPN network or the end of a self condensed siloxane network after the faster, short chain silanes have reacted.

Some commercially available products include DC6341 from Dow Corning and OCTEO from Degussa. A preferred fluorosilane is tridecafluoro octyltriethoxysilane which is available from Sivento as Dynasilane RTM.F 8261. Another suitable fluorosilane is Z-6704 from Dow Corning.

Any number of organo-functional silanes may be used including glycidoxypropyltrimethoxysilanes from such as DC6040 from Dow Corning and GLYMO from Degussa. However, generally the methoxy versions are preferred on a production line.

The concentration of the silane mixture in the aqueous alcohol hydrosylate preferably will be in the range of between 15 and 40%. More preferably the concentration will be in the range of between 25 and 35%.

An upper limit has been discovered regarding the level of hydrosylate liquid that can be added to the inorganic filler in that an unacceptable, wet, poor flowing filler mix is produced if excessive liquid is added. The poor flow and subsequent clumping of the filler gives unacceptable mixing of the hydrosylate when a blender is used to tumble the filler under a hydrosylate spray.

The concentration of the silane hydrosylate when added to the inorganic filler preferably will be in the range of between 1 and 15%. More preferably the concentration will be in the range of between 3 and 7%.

The influence of the silane concentration (in particular GPTMS) on stability has been investigated and it has been found the concentration in alcohol has a major

bearing on self condensation and stability. In general the tendency for self condensation decreases with the corresponding decrease in concentration in an alcoholic hydrosylate.

5 The silane blend may be added directly to the inorganic filler. More preferably the plurality of silanes are suspended or dissolved in an aqueous, alkaline pH adjusted alcohol solution, more preferably a 5% aqueous component in ethanol (in the form of methylated spirit) in order to give a stable solution of a diluted alcoholic silane hydrosylate.

10

 It has been discovered that a critical element in silanising locally available filler in general is the necessity to use a slightly alkaline hydrosylate. Commercial silane manufacturers and suppliers specify acidified silane/alcohol/water hydrosylates to give greater stability of the hydrosylate solution and also to promote the best environment for the production of monomeric silane species in order to give the greatest concentration of silane deposition on the surface.

 It is our contention that a slightly alkaline hydrosylate so made by the addition of a silane to an aqueous alcohol solution and the subsequent adjustment with a suitable amine compound in order to produce a specific blend of monomeric, dimeric and oligomeric silane species allows for a surface treatment process with good consistency and reliability.

 A low water content alkaline environment at a specific pH and silane loading had to be created. Preferably the pH of the mixture during the mixing process is maintained in the range 7 to 10. More preferably the pH is maintained in the range 7 to 8. Most preferably the pH is maintained at close to 8.

 The pH control may be achieved by the addition of volatile amines including primary, secondary or tertiary amines. Other alkaline adjustments may be made with non volatile, mild alkali such as sodium bicarbonate. Preferably control of the pH is achieved by the addition of ammonia to a diluted alcoholic silane

hydrosylate to form an alkaline environment prior to addition to the mixing vessel. While most volatile amines are effective for maintaining the desired pH, many secondary or tertiary amines, such as dimethylethanolamine are less preferable than ammonia due to their weaker base strengths however they may be considered when
5 slower evaporation rates are desirable for open conveyors and requirements for premature pH drift are a concern in hydrosylates that may be left for extended periods.

One unusual feature of the invention is that a comparatively small amount
10 of water is introduced into the system compared to conventional technology which gives a slower, more stable system where the silanes are only partially hydrolysed however the relatively high silane concentration in the hydrosylate of between 25-25 parts w/w compared to a recommendation of around 5 parts w/w by silane manufacturers tends to offset potential stability and produce an unusual silane
15 composition whereby the self condensation reaction may occur.

The composition is chosen such that it is compatible with a silica filled epoxy system and is able to be added directly to a treated or untreated silica, added in-situ into a filled polymer system and/or added directly to a mould that may be
20 baked or is ambient cured.

The preferred system is to apply the aforesaid silane/TN oil premix to the filler after the filler has been treated with the aforesaid plural hydrophobic organo-
functional silane mix.

25

The untreated portions of filler are able to be 'mopped up' by further silane reactions and the silicone oil is adsorbed onto the filler however there are restrictions on the use of silicone oil due to a reduction in free bonding sites of the organo-
functional silane and silicone oil acting as a potential barrier to prevent intimate
30 contact of the resin with filler particles.

The post addition and in-situ additions of wax and silicone combinations outlined in the invention confirmed the short, medium and long term benefits regarding hydrophobicity and improved mould release of the so named technology when used for an application whereby an epoxy-functional filler hydrophobic filler is
5 used in a epoxy polymer baking system.

It was found surprisingly the addition of a highly hydrophobic micronised polyamide wax with a melting point of 135°C such as AQUABEAD 519 gives a stable paste at any loading up to 70% w/w when melted into a non functional
10 dimethyldimethylpolysiloxane mould release silicone oil such as 'Release agent TN' from Wacker chemicals. Release agent TN is claimed to contain methyl groups, phenylethyl groups, and dodecyl groups bonded to silicon.

This enables the successful incorporation of the hydrophobic wax onto a
15 treated or untreated filler to give excellent hydrophobic properties.

A non functional dimethylpolysiloxane oil such as Release agent TN oil gives excellent additional hydrophobic properties and acts as a diluent and carrier to enable a more even distribution of a silane premix including an organo-functional
20 hydrophobic silane blend thus mentioned when added directly to a treated or untreated silica, added in-situ into a filled polymer system and/or added to moulds for baked or ambient cured systems.

In order to further improve hydrophobicity an addition of the silane premix
25 to a silicone oil or other non-volatile diluent is possible when other matters such as strength considerations have been assessed.

The present invention also provides a novel process whereby the silicone oil is used as a carrier for the wax component in order to further treat the silane treated
30 silica to markedly improve the final hydrophobic properties.

It has been found an improvement in hydrophobicity can be realised by the addition of a hydrophobic wax component to the hydrophobically treated silica either directly or in the form of a wax solution melted into a silicone oil. The wax component can be post added to the silica after hydrophobic silane treatment or
5 incorporated as a post addition to the filled polymer.

The present invention demonstrates that a more durable, longer lasting hydrophobic effect is possible than with the use of solely silicon oils due to the use of a stable paste composed of a polyamide wax dissolved in a compatible silicone oil.
10

The paste can be added in-situ directly to the resin system and/or applied directly to the surface of the mould to form a firmly adhering wax/silicone composition that will contribute mould release and hydrophobic properties.

15 Although the use of epoxy silane treated silica and aluminium trihydrate is specified for use in filled cycloaliphatic epoxy voltage insulators due to its recognised contribution to strength and exterior durability, the use of a filler treatment system utilising organo-functional hydrophobic silanes as outlined in this invention has not been claimed.

20 The present invention is claimed to result in a greater hydrophobic efficiency and less possibility for water ingress due to the specific surface treatment of the individual filler fillers before incorporation into the polymer. The major improvement of both hydrophobicity and strength in the invention is due to separate
25 pre-treatment of the inorganic filler with the specified blend of silanes that include a polymer-compatible, organophilic, epoxy-functional silane, a mildly hydrophobic silane and a strongly hydrophobic silane which may, or may not be, fluorinated.

30 US Patent No 3,926,885 discloses that the addition of a blend of polysiloxane, polyether copolymers and OH-terminated polysiloxanes can impart hydrophobic properties to an epoxy resin based system.

However, in general the use of non reactive silicone oils in a thermoset system is not recommended due to the potential plasticising effect and potential weakening of the system by possible migration of the oils to the metal/epoxy reinforcing rod interface on baking.

5

Premature separation of the common linear, non functional silicone oils on storage of the resin is a potential problem in these systems also. It is speculated the use of a unique silicone blend as specified in this patent including cyclised and hydroxyl functional types contribute to compatibility and long term stability in a cycloaliphatic resin system.

10

Similarly JP-A2-305454 describes the use of small amounts of cyclic dimethyl siloxane as an additive in epoxy resin based systems to improve hydrophobic properties. However, hydrophobicity is generally poor.

15

US Patent 6,764,616 describes the use of a selective blend of migratory, non-reactive silicone oils to introduce hydrophobicity to an epoxy system. This selective blend enables compatibility and stability of the oils in the epoxy resin at ambient temperature. The selective migration on baking at 135°C to the exterior of the insulator is due to marginal compatibility in the epoxy resin/hardener/silica mix when baked. Thereafter an acceptable eventual post-bake migration of the oils at ambient temperature will occur upon exterior exposure. This has surprisingly given an acceptable adhesion of the epoxy/silica mix to metal reinforcing hardware with no decrease in strength.

20

25

Due to greater mobility of silicone oil with increasing temperature, accelerated depletion of the silicone reservoir in the insulator can occur upon exposure to extended periods at high ambient temperatures resulting in a reduced life span before hydrophobic effectiveness declines.

30

As dirt, dust and pollution fillers settle on the surface of an insulator the silicone oil will attract the fillers and encapsulate these to give a 'hydrophobic

transfer' effect. Due to the mobile nature of the oil, and loss to dirt and pollution, depletion of the oil is inevitable after the silicone-saturated fillers are lost off the surface.

- 5 Eventually the fillers become saturated, the reservoir of silicone becomes depleted, the surface loses its hydrophobicity and arcing activity is re-established.

10 Indeed, with a demanding environment with a high degree of pollution and contaminants, the inevitable degradation of the surface layer of the insulator the depletion of the silicone oils from the silica-filled epoxy system is accelerated. It is expected differential migration of the various silicone oil components will occur on aging.

15 Due to the high hydrophobic efficiency of silicone oil and its ability to remain liquefied over a large temperature range, it is expected that the silicone oil modified insulator described in US Patent 6,764,616 will offer excellent short to medium term hydrophobicity. This hydrophobicity is expected to be limited to the medium term, particularly after the insulator has weathered and more silicone oil is exposed and released, thus depleting the reserve of silicone oil present in the system.

20

 It has been disclosed that surprisingly strong insulators can be produced and the migratory nature of the silicone oils can be used to good effect with the continual 'sweating' of the oils to the surface of a cured article contributing to an external surface with hydrophobic properties. However, eventually this store of silicone is
25 depleted and hydrophobicity reduces over time.

30 A pure silicone surface as provided by a silicone polymer insulator suffers from silica by-products produced upon arcing that may encourage surface breakdown and reduced hydrophobicity. The present invention offers a far cheaper more durable alternative with a so called 'self healing' property whereby arcing will activate the wax present to improve hydrophobicity.

An inorganic silica or aluminium hydrate filled cycloaliphatic epoxy high voltage insulator system based on the epoxy-functional hydrophobic treated inorganic technology according to the present invention as outlined in the foregoing summary of the invention is expected to be give superior long term results when compared to hydrophobic technology for high voltage insulators based on silicone oils.

It was observed in the context of the present invention that when the wax was chosen to give a melt point at substantially the same temperature as that occurring during the curing cycle of a baking system for a product such as a silica-filled epoxy-polyanhydride product, selective migration of the wax to the outer surface layer of the article occurred which improved mould release properties and subsequent hydrophobic performance.

It was found when a polyamide functional wax such as AQUABEAD 519 was used in a polyanhydride cured baking resin system cured at 135°C that excessive foaming occurred. However, the incorporation of AQUABEAD 519 after melting into Release agent TN at 135°C gave no evidence of foaming at more than ten times the original level.

This enabled a highly effective internal mould release compound that is able to be added in-situ with long lasting hydrophobic properties in the finished product.

As described in US Patent 5,212,218 'self-healing' hydrophobic properties can be imparted to epoxy resins for use in voltage insulators by addition of a hydrophobic wax with a melting point above 27°C. This is present in discrete, suspended droplets to form a discontinuous phase. Lower dust attraction is possible compared to the use of a silicone oil hydrophobe and the technology has the ability to melt and encapsulate the surface dust during increased arcing activity. US Patent 6,548,763 also describes 'self healing' electrical insulators that consist of an encapsulated hydrophobe similar in principle to US Patent 5,212,218 whereby the encapsulated hydrophobe is released under thermal and/or oxidative degradation of

the surface which occurs with arcing or 'flash over' of the insulator. An example is given whereby a silicone oil is encapsulated in an uncured melamine formaldehyde resin.

5 A high degree of dust and pollution fillers may be deposited before arcing occurs which can increase the probability of an excessive 'flash over' occurring. The ability of the system to cope with this may be compromised.

10 The present invention offers a preventative rather than a repair system. The self healing system of US 6,548,763 is only activated when arcing occurs. However, significant damage to insulators or other equipment may occur before the wax is 'activated'.

15 Arcing across the face of the insulator can have a serious effect on the insulator performance due to the formation of conductive carbon deposits which may form a permanent conductive path along the surface of the insulator thereby shortening the lifespan of the insulator.

20 Another aspect of the present invention allows for a process for hydrophobically treating an arc resistant, highly water absorbing filler such as aluminium trihydrate for use in a cycloaliphatic epoxy high voltage insulator in order to enable the introduction of self healing, arc resistant properties while improving or retaining long term hydrophobic properties of the final system when exposed to exterior weathering.

25 Aluminium trihydrate (commonly referred to as ATH or gibbsite) has the chemical formula $\text{Al}(\text{OH})_3$ and is typically used as a filler or flame retardant in plastics and other polymers. The chemical treatment of ATH products has typically been accomplished via the addition of the neat treatment additives to the ATH in dry
30 filler form with good blending in a solids/liquid blending device with the optional use of heat.

It is known from US Patent Nos. 2,997,526, 2,997,527, 4,206,066 and 2,997,528, and 4,668,718, the disclosures of which are incorporated herein by reference, that polymeric insulating materials can be rendered highly resistant to tracking by the use of aluminium trihydrate as an anti-tracking filler due to the
5 absence of the conductive carbonaceous path that is left by organic resins such as the epoxy system described herein.

The effect on final hydrophobicity of systems by the addition of an untreated grade of aluminium trihydrate may be compromised due to its inherent
10 water absorbing (hydrophilicity) properties and alkaline nature.

The use of aluminium trihydrate is limited due to the hydrophilic nature of the filler, the increased cost when compared to other inorganic based fillers, a poorer strength and a poorer viscosity when incorporated at the same loading.
15

US Patents 3,511,698, 5,59,080, 5,691,407, 5,994,461, 6,251,990 and 5,691,407 describe systems composed of aluminium trihydrate and/or inorganic filled silicone rubber with inherent hydrophobic properties.

A major consideration with the present invention is the ability to use 'self healing' technology including aluminium trihydrate without suffering a loss in hydrophobic properties. Indeed the same hydrophobic pre-treatment used with aluminium trihydrate fillers in the present invention may be used to hydrophobically pre-treat other inorganic fillers and ensure reduction or minimization of a potential
20 weakness due to inherent hydrophilicity of the aluminium trihydrate or other
25 inorganic fillers.

US Patent 4,749,824 describes a process whereby a unique aluminium trihydrate arc resistant silicone elastomer is used in conjunction with a specific
30 insulator design to give excellent performance under wet conditions. The present invention offers acceptable arc resistant performance under wet conditions without

the use of expensive aluminium trihydrate although a further improvement is offered by the invention whereby a hydrophobically treated aluminium trihydrate is used.

US Patent 3,647,742 describes a process whereby aluminium trihydrate is
5 treated with an epoxy silane composition in order to improve its tensile strength, percent elongation and toughness in general for a cycloaliphatic epoxy system.

Silicone 'membrane' coatings may be applied by the manufacturer of
insulators on the production line. These coatings are commonly applied by dipping
10 an epoxy/silica or porcelain insulator in the coating after the product has been baked or cured.

Compared to a solid silicone insulator the cycloaliphatic epoxy-
polyanhydride systems enable significant cost savings due to the use of a stronger,
15 cheaper epoxy-silica base under the silicone encapsulation. However, the use of the silicone encapsulation technology is inhibited by an increased raw material cost to the article and the storage and purchase of further raw materials.

Modifications of production lines are required to accommodate the further
20 processes of dipping, drying and stacking the parts. In order to ensure acceptable bonding or compatibility between the silicone coating and the article there is a requirement for a compatible, yet potentially less effective release agent. Limited hydrophobic durability is expected due to a low migratory silicone reservoir compared to a solid silicone insulator and inconsistent film build over the surface of
25 the article.

The present invention offers a method of introducing a durable hydrophobic coating to the surface of the insulator without a further application step in the manufacturing process or out in the field with a post application.
30

US Patent 4,418,171 describes a process whereby a blend of silicone elastomer and incompatible silicone are moulded into a article whereby the oil will

migrate to the surface and present hydrophobic properties over the cured silicone elastomer. The invention in that patent relies on a similar principle of a partially compatible silicone or wax that will preferentially migrate when the article cures to give a surface with hydrophobic properties. However, the present invention offers a more permanent solution over an epoxy based system whereby the migratory oil will bond to the epoxy and present a more durable hydrophobic 'skin' on the insulator.

Attempts to overcome the aforementioned problems with insulators and to present a hydrophobic surface that will prevent water ponding and subsequent dirt pickup have included the post addition of silicone gel in the field. These post addition silicone gel applications are very time consuming, labour intensive and expensive.

US Patent 4,011,168 describes the production of a silicone grease suitable for hydrophobic post treatment of silicone, epoxy or ceramic insulators. US Patent 4,177,322 describes the use of a suitable silicone fluid for post application either by the manufacturer of the insulators or by application in the field. However, this practice is expensive, unreliable and time consuming. Another aspect of the present invention offers a method of producing a durable insulator with no need for post additions when installed.

We have found the incorporation of a polyamide modified wax at any level above 0.05% into a epoxy/polyanhydride/silica composition used for voltage insulators will give rise to a vigorous foaming when the composition is heated to the wax's melting point of 135°C which is also the temperature required in order to cure the article. The foaming was found to be caused by an interaction of the polyamide modified wax with the polyanhydride epoxy hardener and it limited the amount of wax incorporated to less than 0.05% on the final silica-filled product.

The effectiveness of the wax in relation to the final hydrophobic properties of the finished article ensured some improvement in hydrophobicity at this low level. However, one object of the present invention is to increase the wax level in order to

improve the mould release properties and subsequent hydrophobicity of the finished article.

The use of a non functional grade of silicone oil such as 'Wacker TN oil' enabled a stable highly water repellent polyamide wax paste to be introduced which heretofore would not have been possible due to a preferential reaction of the polyamide wax with the polyanhydride hardener.

Thus another aspect of the present invention offers a method of improving the release from a mould for an epoxy resin based system and offering a far more durable, effective hydrophobic effect by use of a plurality of undiluted silanes including methyl trimethoxysilane, octyl triethoxysilane and glycidoxy propyl trimethoxysilane in the approximate weight ratio 20:60:20 mixed with a dimethylpolysiloxane such as Release Agent TN from Wacker chemicals at a loading of between 5-30 parts w/w.

An epoxy reactive mould release compound can be applied to the mould used for an anhydride cured cycloaliphatic epoxy high voltage insulator to form a durable silicone composition on the finished product that will contribute to long term hydrophobicity.

According to another aspect of the present invention there is provided a process for producing strongly hydrophobic epoxy-functional fillers, including silica, by admixing one or more of said fillers with a plurality of silanes, said plurality of silanes including at least one mildly hydrophobic silane, at least one strongly hydrophobic silane, and at least one cross-linking epoxy-functional silane, said plurality of silanes being in the form of an alkaline hydrosylate to produce a hydrophobic epoxy-functional filler. This filler demonstrates significantly improved compatibility, reduced viscosity, improved, and in some instance exceptional, strength, electrical, exterior performance and hydrophobic properties when incorporated into a heat cured epoxy-anhydride system for use in voltage insulators.

According to another aspect of the present invention there is provided a process for incorporating the aforesaid hydrophobic, epoxy-functional fillers into the liquid portion of an epoxy or polyanhydride resin system for use in voltage insulators to produce a system that has exceptional anti-settling behaviour and storage stability
5 when stored.

According to another aspect of the present invention there is provided a process for imparting hydrophobicity to a filled, cycloaliphatic epoxy insulator heat cured with a polyanhydride hardener produced by any of the foregoing methods and
10 including silica flour at a loading of between 30-90 percent, and formulations and products, including moulded products, incorporating such compositions.

According to another aspect of the present invention there is provided a process for treating the aforesaid hydrophobic, epoxy-functional fillers with a
15 functional dimethylpolysiloxane silicone oil at a loading of between 0.01-10 parts by weight in order to improve the hydrophobicity.

According to another aspect of the present invention there is provided a process for treating the aforesaid hydrophobic, epoxy-functional fillers with a non
20 functional dimethylpolysiloxane silicone oil at a loading of between 0.01-10 parts by weight in order to improve the hydrophobicity.

According to another aspect of the present invention there is provided a process for treating the aforesaid hydrophobic epoxyfunctional fillers such as silica
25 with a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight.

According to another aspect of the present invention there is provided a process for treating the aforesaid hydrophobic epoxyfunctional fillers such as silica
30 with (1) a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight and/or (2) a PTFE wax at a loading of between 0.01-10 parts by weight.

According to another aspect of the present invention there is provided a process for treating the aforesaid hydrophobic epoxyfunctional fillers such as silica with (1) a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight and/or (2) a PTFE wax at a loading of between 0.01-10 parts by weight
5 and/or (3) a dimethylpolysiloxane silicone oil at a loading of between 0.01-10 parts by weight.

According to another aspect of the present invention there is provided a process for treating the aforesaid hydrophobic epoxyfunctional fillers such as silica
10 with (1) a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight and/or (2) a PTFE wax at a loading of between 0.01-10 parts by weight and/or (3) a dimethylpolysiloxane silicone oil at a loading of between 0.01-10 parts by weight and/or (4) a dimethylpolysiloxane silicone oil with functional groups at a loading of between 0.01-10 parts by weight.

15

According to another aspect of the present invention there is provided a process for incorporation of a wax with a melting point approaching the gelation point of a heat cured cycloaliphatic epoxy resin system including the step of melting the wax into the silicone oil component at an elevated temperature in order to
20 successfully incorporate the wax and silicone blend into the resin mix.

According to another aspect of the present invention there is provided a process for the use of a hydrophobic wax and silicone oil composition in a heat cured cycloaliphatic epoxy resin based high voltage insulator such that the final product
25 gives a durable hydrophobic layer on the surface of the insulator due to selective migration of a wax and silicone compound by heat curing of the epoxy resin with a polyanhydride hardener.

According to another aspect of the present invention there is provided a
30 process for the use of a hydrophobic wax and silicone oil composition in a heat cured cycloaliphatic epoxy resin based high voltage insulator such that the final product has 'self healing' properties when exposed to arcing whereby the wax will melt and

form a hydrophobic track along the surface of the insulator to inhibit further deposition of dirt or a conductive track formed by the combined effects of pollution and water sheeting.

5 According to another aspect of the present invention there is provided a process for the use of polytetrafluoroethylene (PTFE) wax to be dispersed into the resin/silica mix of a cycloaliphatic epoxy resin which enables long term hydrophobic properties to be achieved due to its superior exterior durability and UV resistance and which enables 'self healing' properties of the insulator when exposed to arcing
10 whereby the wax will melt and form a hydrophobic track along the surface of the insulator to inhibit further deposition of dirt or a conductive track formed by water sheeting.

 According to another aspect of the present invention there is provided a
15 process for the production of a hydrophobic wax/silicone additive including the step of melting a hydrophobic wax or waxes including PTFE into a reactive or non reactive, dimethylpolysiloxane silicone oil at a wax-silicone ratio of between 0.2 to 50%.

20 According to another aspect of the present invention there is provided a process for the production of a hydrophobic epoxy-functional wax/silicone additive including the step of melting a hydrophobic wax or waxes including PTFE into a blend of epoxy silane and non reactive, dimethylpolysiloxane silicone oil at a wax-silicone ratio of between 0.2 to 50%.

25 According to another aspect of the present invention there is provided a process for treating the aforesaid hydrophobic epoxyfunctional fillers for use in epoxy resin systems in voltage insulators with the aforesaid wax/silicone additive at a loading of between 0.1 and 10 % in order to improve hydrophobic properties.

30 According to another aspect of the present invention there is provided a process for imparting hydrophobicity and enhanced release from the mould to

voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener including the step of the in-situ addition of the aforesaid wax/silicone additive.

5 According to another aspect of the present invention there is provided a process for imparting hydrophobicity and enhanced release from the mould to voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener by the in-situ addition into the liquid of (1) a hydrophobic epoxyfunctional plurality of silanes and
10 (2) the aforesaid hydrophobic wax dispersed in a dimethylpolysiloxane silicone oil.

 According to another aspect of the present invention there is provided a process for imparting hydrophobicity and enhanced release from the mould to voltage insulators composed of an epoxy-functional hydrophobic silica filled into a
15 cycloaliphatic epoxy resin system with a polyanhydride hardener by the in-situ addition into the liquid of (1) a hydrophobic epoxyfunctional plurality of silanes and (2) a dimethylpolysiloxane silicone oil.

 According to another aspect of the present invention there is provided a
20 process for imparting hydrophobicity and enhanced release from the mould to voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener by application to the mould of a blend consisting of (1) a hydrophobic epoxyfunctional plurality of silanes and (2) a dimethylpolysiloxane silicone oil.

25 According to another aspect of the present invention there is provided a process for imparting hydrophobicity and enhanced release from the mould to voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener by the in-situ
30 addition of (1) a micronised hydrophobic wax and (2) a PTFE wax.

According to another aspect of the present invention there is provided a process for imparting hydrophobicity and enhanced release from the mould to voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener by the in-situ addition of (1) a micronised hydrophobic wax and (2) a PTFE wax and (3) a dimethylpolysiloxane silicone oil.

According to another aspect of the present invention there is provided a process for imparting hydrophobicity and enhanced release from the mould to voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener by the in-situ addition of (1) a micronised hydrophobic wax and (2) a PTFE wax and (3) a dimethylpolysiloxane silicone oil and (4) a dimethylpolysiloxane silicone oil with functional groups.

According to yet another aspect of the present invention there is provided a process for imparting hydrophobicity to fillers of aluminium trihydrate filler for use in an arc resistant cycloaliphatic epoxy insulator, said method including the step of mixing said fillers with a silane mixture composed of at least one mildly hydrophobic silane, at least one strongly hydrophobic silane, and at least one cross-linking epoxy-functional silane, at controlled alkaline pH.

The process for hydrophobically treating aluminium trihydrate for use in an anhydride-cured cycloaliphatic epoxy high voltage insulator enables the introduction of self healing, arc resistant properties while improving or retaining long term hydrophobic properties of the final system when exposed to exterior weathering.

According to another aspect of the present invention there is provided a process for the incorporation of an arc resistant composition consisting of at least one hydrophobically treated mineral filler, or any blends thereof, with hydrophobically treated aluminium trihydrate in an anhydride cured cycloaliphatic epoxy resin based electrical insulator with long term hydrophobic properties.

DESCRIPTION OF PREFERRED EMBODIMENTS

In order that the invention may be more readily understood reference is
5 made to some non-limiting preferred embodiments illustrating some aspects of the
present invention.

WORKED EXAMPLE 1

10 An alcoholic silane hydrosylate containing methyl trimethoxysilane, octyl
triethoxysilane and glycidoxy propyl trimethoxysilane in the approximate weight
ratio 20:60:20 is prepared by the addition of the plurality of silanes to ethanol to give
a total silane concentration of approximately 5% w/w.

15 25% grade ammonia is then diluted with water to give a 5% solution. This is
then added to the hydrosylate to give a final concentration of 0.25% ammonia (w/w)
in the hydrosylate. The pH of the resultant mixture will be in the range 7-8.

One tonne of silica filler is added to a horizontal mixer equipped with a
20 variable speed ribbon blender. Mixing is commenced and between 30 kg and 70 kg
of the alkalinized silane hydrosylate is then sprayed onto the inorganic flour via a
sprinkler system. Mixing continues at a temperature of 20°C for 30-90 minutes until
the inorganic filler is thoroughly coated with the mixture of silanes.

25 The treated inorganic filler is transferred by an auger to a drier at a
temperature of between 80°C and 110°C until all solvent is removed from the treated
inorganic filler.

The following table sets out a preferred formulation for hydrophobically
30 treating inorganic filler with an epoxy-functional silane. It shows preferred % mass
ratios for the named silanes as well as the makeup of a preferred alkaline
hydrosylate.

Component	% of Treatment Formulation	% of Hydrolyate	% of Silane Mix
<u>Silica</u>			
(Grade 350G)	95.00		
<u>Hydrolysate</u>			
IMS	3.52	70.2	
Ammonia (25%)	0.05	0.95	
Water	0.17	3.4	
Glycidoxypropyl Trimethoxysilane	0.23	4.55	17.9
Octyl triethoxysilane	0.76	15.2	59.7
Methyl trimethoxysilane	0.29	5.7	22.4
Totals	100.02	100	100

5 The mixing vessel can be a horizontal mixer provided with mixing blades and speed controls to vary the speed of mixing. It should be suitable for "filler" tumbling and must be an enclosed vessel with small venting means to minimise powder and solvent loss but must be capable of dispensing to an auger or some other suitable conveyor.

10 The mixing vessel must be provided with an internal sprinkler system for addition of the silane hydrolysate. Preferably the method of mixing is tumbling in a ribbon blender with variable speed.

15 The treated silica filler is dried in the plant at a temperature of between 40°C and 110°C, more preferably between 80°C and 110°C, for 30-40 seconds to

give a loss on dry of at least 0.03% when a 100 gram test sample is reweighed after 1 hour at 140°C.

5 It has been discovered the input of at least 250°C is required to give a fully reacted silica with maximum hydrophobic properties when dried for 30-40 seconds.

10 For a dry cycle of 80-110°C a post cure of up to a week is required to attain full hydrophobic properties as assessed by evaluating the comparative water contact angle and methanol/water tolerance with fully hydrophobic samples.

15 It is preferred that treated silica filler be absolutely dry after processing to minimize defects in parts subsequently made. The drying process currently used employs a heated air duct where the treated silica flour is pneumatically conveyed and dried.

20 The silica flour is subsequently separated from the air stream by a cyclone, through a vortex and through a filter.

The treated silica thus produced has outstanding hydrophobic properties and shows no sign of water absorption after submersion in water after three months.

25 An analytical test using a aqueous pretreatment of sodium thiosulphate followed by the addition of a dilute bromothymol blue indicator solution showed a strong presence of organo-functional epoxy groups.

30 Indications that the treatment of the silica filler was successful include a free flowing filler with the absence of lumps, no thickening on addition of the filler to the epoxy resin, good filler dispersion in the resin mix, low viscosity and low surface tension of the resin mix, improved final strength test, improved water soak strength test, and minimal water absorption on extended pressurised soaking.

- 75 -

As outlined in the foregoing example, the epoxy-functional hydrophobic silica thus made was used as a filler in a polyanhydride cured epoxy based polymer that was moulded into high voltage insulators.

5 The improvement in strength and long term hydrophobic properties confirmed the successful utilisation of the filler thus treated.

EXAMPLE 2 - VOLTAGE INSULATOR

10

Using a blade mixer, 600 kg of hexahydrophthalic acid diglycidyl ester (epoxy value: 5.6-6.2 val/kg) is mixed with 520 kg of a hardener mixture consisting of 70.0 parts by weight of hexahydrophthalic anhydride and 30.0 parts by weight of methylhexahydrophthalic anhydride, 4 kg of benzyldimethylamine and 2500 kg of
15 the aforesaid hydrophobic, epoxy silane treated silica filler over 30 min at 30°C.

A further 200 kg of the aforementioned epoxy resin and 200 kg of the aforementioned anhydride hardener are added and the mixture is given a further mixing for 20 minutes at 60°C.

20

This mixture is then briefly degassed at about 10 mbar.

COMPARISON EXAMPLE 2A - VOLTAGE INSULATOR

25

Using a blade mixer, 600 kg of hexahydrophthalic acid diglycidyl ester (epoxy value: 5.6-6.2 val/kg) is mixed with 520 kg of a hardener mixture consisting of 70.0 parts by weight of hexahydrophthalic anhydride and 30.0 parts by weight of methylhexahydrophthalic anhydride, 4 kg of benzyldimethylamine and 2500 kg of epoxy silane treated silica filler over 30 min at 60°C.

30

A further 200 kg of the aforementioned epoxy resin and 200 kg of the aforementioned anhydride hardener are added and the mixture is given a further mixing for 20 minutes at 60°C.

5 This mixture is then briefly degassed at about 10 mbar.

In each instance the dried treated silica flour is mixed with epoxy resin and that mixture is moulded under pressure to form insulators or other moulded products for which hydrophobicity is a required or highly desired property.

10

The surfaces of the resulting insulators are smooth with a slightly higher sheen than normally seen. Water does not wet them but forms beads which can be readily run off. It is recognised the initial hydrophobicity before the insulator is exposed is due to the presence of silicone oil release agent on a smooth, resin-rich surface. The long lasting hydrophobic properties imparted by the incorporation of hydrophobic silica filler are not realised until the insulator has been exposed to some form of degradation in order to expose the hydrophobic silica fillers.

15

APPLICATION EXAMPLE 3 - VOLTAGE INSULATOR

20

Support insulators are produced by the following procedure.

The mixtures prepared as beforehand are processed by the pressure gelation method and injected separately into metal moulds heated to 140°C. The moulds have previously been treated with demoulding agents.

25

After 20 min the moulded article is removed from the mould and postcured for 10 h at 140°C.

30

Evaluation is conducted by observing the beading action of water and comparative penetration on the surface of the insulators when sprayed with water.

Samples of the insulators are solvent washed and lightly abraded in order to remove the influence of the residual mould release compound from the surface of the insulator before placing them in an accelerated weathering tester.

5 The insulators prepared from the novel composition show significantly improved hydrophobic properties and evidence of water beading after 1700 hours in an accelerated weathering tester compared to a standard epoxy silane treated silica sample that demonstrated water sheeting with no evidence of beading.

10 The support insulators have comparative cantilever strength than the insulator prepared from the standard epoxy silane produced product.

 Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", is to be understood to imply the inclusion of a stated integer or
15 step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

 The reference to any prior art in this specification is not, and should not, be
20 taken as an acknowledgment or any form or suggestion that the prior art forms part of the common general knowledge in Australia or elsewhere.

 Finally, it is to be understood that the foregoing description refers merely to preferred embodiments of the invention, and that variations and modifications will be
25 possible thereto without departing from the spirit and scope of the invention.

CLAIMS

1. A process for imparting hydrophobicity to particles, said process
5 including the step of mixing said particles with a blend or mixture of a plurality of silanes at an alkaline pH.
2. A process as claimed in claim 1 wherein said blend of a plurality of
silanes includes at least one mildly hydrophobic silane, at least one strongly
10 hydrophobic silane, and at least one functional silane.
3. A process for imparting hydrophobicity to particles, as claimed in
either claim 1 or claim 2, wherein said particles are selected from fillers, said fillers
including at least one material selected from the group consisting of semimetal
15 oxides and metal oxides, silica (aerosil, quartz, quartz filler, synthetic silica flour),
oxides of zinc, titanium, aluminium, silicon, zirconium, lead, chromium and iron,
aluminium trihydrate, semimetal nitrides and metal nitrides (including but not limited
to silicon nitride, boron nitride and aluminium nitride), semimetal carbides and metal
carbides (including but not limited to SiC), metal carbonates (including but not
20 limited to dolomite, chalk, CaCO₃), calcined clay, delaminated kaolin clay, metal
sulphates (baryte, gypsum), mineral fillers and natural or synthetic minerals,
including the group comprising zeolite, talcum, mica, kaolin, wollastonite, bentonite,
metal filler, glass filler, glass beads.
- 25 4. A process for imparting hydrophobicity to one or more fillers of
inorganic material (including non-mineral material, including carbon black) with a
blend of a plurality of silanes, said process including admixing at least one mildly
hydrophobic silane, at least one strongly hydrophobic silane, and at least one organo-
functional silane with said one or more fillers under controlled alkaline conditions.
30
5. A process for imparting hydrophobicity to at least one filler, said
method including the steps of admixing a slurry containing said at least one filler

with a blend of a plurality of silanes under controlled alkaline pH in a mixing vessel, and subsequently drying the treated said at least one filler.

5 6. A process for treatment of inorganic fillers including the deposition of both organo-functional and hydrophobic groups on the surface of the said at least one inorganic filler by a blend of a plurality of silanes, their hydrosylates or resulting condensates.

10 7. A process for imparting hydrophobicity to an inorganic filler or a plurality of inorganic fillers, wherein a blend of a plurality of silanes is added to said inorganic filler or said plurality of inorganic fillers, in the form of an alkaline hydrosylate of said blend of a plurality of silanes in a mixing vessel and subsequently drying the treated said inorganic filler or plurality of said inorganic fillers.

15 8. A process for imparting hydrophobicity to one or more inorganic fillers, said method including the step of mixing said one or more inorganic fillers with a blend of at least one mildly hydrophobic silane, at least one strongly hydrophobic silane, and at least one organo- functional silane, at controlled alkaline pH.

20

 9. A process as claimed in any one of claims 1 to 8 wherein said blend of a plurality of silanes is admixed with a volatile aqueous alcohol blend adjusted to an alkaline pH in the range of 7 to 10 by the addition of a volatile amine prior to the admixing of the resultant hydrosylate with the said one or more fillers.

25

 10. A process claimed in any one of claims 1 to 9 for the production of a range of hydrophobic fillers compatible with a broad range of organic polymer systems by the selective substitution of organo-functional silanes.

30

 11. A process as claimed in any one of claims 2 to 10 wherein the at least one organo-functional reactive silane is selected from the group consisting of epoxy

silanes, aminosilanes, isocyanatosilanes, methacryl silanes, mercaptosilanes and vinylsilanes, not excluding alkyl, phenyl or fluoroalkyl modified moieties.

12. A process as claimed in any one of claims 2 to 11 wherein the at least
5 one strongly hydrophobic silane is selected from the group consisting of alkyl and fluoroalkyl silanes with a carbon chain length of up to and including twelve carbon atoms either in a linear, cyclised, aromatic or branched structure, not excluding organo-functional modified moieties.

10 13. A process as claimed in any one of claims 2 to 12 wherein the at least one mildly hydrophobic silane is selected from the group consisting of alkyl silanes with a carbon chain length of up to and including six carbon atoms either in a linear, cyclised, aromatic or branched structure, not excluding organo-functional modified moieties.

15

14. A process as claimed in any one of claims 2 to 13 wherein the concentration of the said at least one organo-functional silane in the silane blend is between 5 and 50% by weight and preferably between 10 and 30%.

20 15. A process as claimed in any one of claims 2 to 14 wherein the concentration of the said at least one strongly hydrophobic silane in the silane blend is between 10 and 80% by weight and preferably between 50 and 70%.

25 16. A process as claimed in any one of claims 2 to 14 wherein the concentration of the said at least one mildly silane in the hydrophobic silane blend is between 5 and 50% by weight and preferably between 10 and 30%.

30 17. A process as claimed in any one of claims 1 to 16 wherein the silane hydrosylate is added to the one or more fillers at a range between 1 and 50% by weight and preferably between 3 and 20% by weight on the basis of the one or more filler to be treated.

18. A process as claimed in any one of claims 1 to 17 wherein the concentration of silanes in the hydrosylate is between 1 and 50 % by weight and preferably between 15 and 40%.

5 19. A process as claimed in any one of claims 9 to 18 wherein the concentration of amine used for pH adjustment in the hydrosylate is between 0.0 and 5% by weight and preferably between 0.1 and 2.0 %.

10 20. A process as claimed in any one of claims 9 to 19 wherein the concentration of water in the hydrosylate is between 1 and 50% by weight and preferably between 2 and 10%.

15 21. A process as claimed in any one of claims 9 to 20 wherein the adjustment of the pH between 7 to 10 of the hydrophobic silane hydrosylate is by addition of aqueous solutions of primary, secondary and/or tertiary amine compounds.

20 22. A process as claimed in claim 21 wherein said primary, secondary and/or tertiary amine compounds are selected from ammonia and dimethylethanolamine.

25 23. A process for imparting hydrophobicity to at least one inorganic filler under alkaline conditions wherein the pH of a hydrosylate containing a blend of a plurality of silanes is maintained in the range of 7 to 8 by the addition of a volatile amine to said hydrosylate prior to the admixing of said hydrosylate with the at least one inorganic filler.

30 24. A process for imparting hydrophobicity to at least one inorganic filler, as claimed in claim 22, wherein the amount of the plurality of silanes is from 0.1 to about 5.0 weight percent on a dry mineral basis.

25. A composition consisting essentially of at least one hydrophobically treated inorganic filler produced by a process as claimed in any one of claims 1 to 24.

26. A resin-containing composition containing at least one
5 hydrophobically treated inorganic filler produced by a process as claimed in any one of claims 1 to 24, at a loading of between about 10 to about 90 parts by weight per one hundred parts by weight of resin .

27. Formulations and products, including moulded products,
10 incorporating a resin-containing composition as claimed in claim 26.

28. A resin-containing composition containing one or more hydrophobic organo-functional silane treated fillers, as claimed in claim 26, and additionally, one or more waxes and/or silicone oils.

15
29. A process for the manufacture of filled polymer products (including high voltage insulators), said filled polymer products containing hydrophobic epoxy-functional silane treated fillers produced according to a process as claimed in any one of claims 1 to 24, and including silica flour and wax and/or silicone oil, wherein an
20 additional step of post addition of a silane, silicone oil and/or wax component to the filled polymer products takes place.

30. Compositions consisting essentially of hydrophobic organo-functional silane treated fillers, as produced by a process claimed in any one of claims 1 to 28,
25 said filler including silica flour, and wax and/or silicone oil, at a loading of between 30-70 percent by weight.

31. Formulations and products, including moulded products,
incorporating, or formed from, compositions as claimed in claim 30.

30

32. A process, wherein one or more of a hydrophobic organo-functional silane treated filler, as prepared by a process as claimed in any one of claims 1 to 24,

is subjected to the addition of a micronised hydrophobic wax at a loading of between 0.01 and 10 parts by weight.

33. A process wherein one or more hydrophobic organo-functional silane
5 treated fillers, as prepared by a process as claimed in any one of claims 1 to 24, is
subject to the addition of (1) a micronised hydrophobic wax at a loading of between
0.01 and 10 parts by weight and/or (2) a PTFE wax at a loading of between 0.01 and
10 parts by weight.

10 34. A process wherein one or more of the aforesaid hydrophobic organo-
functional silane treated fillers, as prepared by the process as claimed in any one of
claims 1 to 24, is subjected to the addition of dimethylpolysiloxane silicone oil at a
loading of between 0.01 and 10 parts by weight.

15 35. A process wherein one or more of the aforesaid hydrophobic organo-
functional silane treated fillers, as prepared by the process as claimed in any one of
claims 1 to 24, is subjected to the addition of (1) a dimethylpolysiloxane silicone oil
at a loading of between 0.01 and 10 parts by weight and/or (2) a
20 dimethylpolysiloxane silicone oil provided with functional groups at a loading of
between 0.01 and 10 parts by weight.

36. A process wherein one or more of hydrophobic organo-functional
silane treated fillers, as prepared by a process as claimed in any one of claims 1 to
24, is subjected to the addition of one of more of (1) a micronised hydrophobic wax
25 at a loading of between 0.01 and 10 parts by weight, (2) a PTFE wax at a loading of
between 0.01 and 10 parts by weight, (3) a dimethylpolysiloxane silicone oil at a
loading of between 0.01 and 10 parts by weight, and (4) a dimethylpolysiloxane
silicone oil with functional groups at a loading of between 0.01 and 10 parts by
weight.

30

37. A process for the production of a hydrophobic treatment component including melting a hydrophobic wax and/or waxes into a dimethylpolysiloxane silicone oil at a loading of between 0.01-90 parts by weight.
- 5 38. A process for the production of a hydrophobic treatment component including melting a hydrophobic wax and/or waxes into a dimethylpolysiloxane silicone oil with functional groups at a loading of between 0.01- 90 parts by weight.
- 10 39. A process for the production of a hydrophobic treatment component including melting a hydrophobic wax and/or waxes into a dimethylpolysiloxane silicone oil at a loading of between 0.01- 90 parts by weight.
- 15 40. A process for producing strongly hydrophobic, epoxy-functional fillers including silica by admixing said fillers with a plurality of silanes including at least one mildly hydrophobic silane, at least one strongly hydrophobic silane, and at least one cross-linking epoxy-functional silane in the form of an alkaline hydrosylate.
- 20 41. A process for altering the hydrophobicity of a hydrophobic epoxy-functional filler, produced according to claims 40, including the additional step of adding either a functional dimethylpolysiloxane silicone oil at a loading of between 0.01 and 10 parts by weight or a non-functional dimethylpolysiloxane silicone oil at a loading of between 0.01 and 10 parts by weight.
- 25 42. A process for altering the hydrophobicity of a hydrophobic epoxy-functional filler, produced according to claim 40, said process including the additional step of adding one or more of a micronised hydrophobic wax, a PTFE wax, a dimethylpolysiloxane silicone oil, and a dimethylpolysiloxane silicone oil functional groups, each being at a loading of between 0.01 and 10 parts by weight.
- 30 43. A process for treating the aforesaid hydrophobic epoxyfunctional fillers by adding a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight.

44. A process for treating the aforesaid hydrophobic epoxyfunctional fillers such as silica by adding (1) a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight and/or (2) a PTFE wax at a loading of between 0.01-10 parts by weight.

5

45. A process for treating the aforesaid hydrophobic epoxy-functional fillers such as silica by adding (1) a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight and/or (2) a PTFE wax at a loading of between 0.01-10 parts by weight (3) a dimethylpolysiloxane silicone oil at a loading of between 0.01-10 parts by weight.

10

46. A process for treating the aforesaid hydrophobic epoxy-functional fillers such as silica by adding one or more of (1) a micronised hydrophobic wax at a loading of between 0.01-10 parts by weight, (2) a PTFE wax at a loading of between 0.01-10 parts by weight, (3) a dimethylpolysiloxane silicone oil at a loading of between 0.01-10 parts by weight, (4) a dimethylpolysiloxane silicone oil with functional groups at a loading of between 0.01-10 parts by weight.

15

47. A process for incorporation of a wax with a melting point approaching the gelation point of a heat cured cycloaliphatic epoxy resin system including melting the wax into the silicone oil component at an elevated temperature in order to incorporate the wax and silicone blend into the resin mix.

20

48. A process for the production of a hydrophobic wax/silicone additive including melting a hydrophobic wax or waxes including PTFE into a reactive or non reactive, dimethylpolysiloxane silicone oil at a wax-silicone ratio of between 0.2 and 50%.

25

49. A process for the production of a hydrophobic epoxy-functional wax/silicone additive including melting a hydrophobic wax or waxes including PTFE into a blend of epoxy silane and non reactive, dimethylpolysiloxane silicone oil at a wax-silicone ratio of between 0.2 to 50%.

30

50. A process for treating the aforesaid hydrophobic epoxy-functional fillers for use in epoxy resin systems in voltage insulators by adding the said hydrophobic wax/silicone additive product, as claimed in claim 48, at a loading of
5 between 0.1 and 10%.

51. A process for imparting hydrophobicity to, and enhanced release from a mould of, voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener
10 including in-situ addition of the said hydrophobic wax/silicone additive product as claimed in claim 48.

52. A process for imparting hydrophobicity to, and enhanced release from a mould of, voltage insulators composed of an epoxy-functional hydrophobic silica
15 filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener including in-situ addition into the preset liquid composition of (1) a hydrophobic epoxy-functional plurality of silanes and/or (2) the said hydrophobic wax dispersed in a dimethylpolysiloxane silicone oil.

20 53. A process for imparting hydrophobicity to, and enhanced release from a mould of, voltage insulators composed of an epoxy-functional hydrophobic silica filled into a liquid cycloaliphatic epoxy resin system with a polyanhydride hardener including in-situ addition into the liquid of (1) a hydrophobic epoxy-functional plurality of silanes and for (2) a dimethylpolysiloxane silicone oil.

25

54. A process for imparting hydrophobicity to, and enhanced release from a mould of, voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener including application to the mould of a blend consisting of (1) a hydrophobic
30 epoxyfunctional plurality of silanes and for (2) a dimethylpolysiloxane silicone oil.

55. A process for imparting hydrophobicity to, and enhanced release from a mould of, voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener including in-situ addition of (1) a micronised hydrophobic wax and/or (2) a PTFE wax.

56. A process for imparting hydrophobicity to, and enhanced release from a mould of, voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener including in-situ addition of (1) a micronised hydrophobic wax and/or (2) a PTFE wax and/or (3) a dimethylpolysiloxane silicone oil.

57. A process for imparting hydrophobicity to, and enhanced release from a mould of, voltage insulators composed of an epoxy-functional hydrophobic silica filled into a cycloaliphatic epoxy resin system with a polyanhydride hardener including in-situ addition of (1) a micronised hydrophobic wax and/or (2) a PTFE wax and/or (3) a dimethylpolysiloxane silicone oil and/or (4) a dimethylpolysiloxane silicone oil with functional groups.

58. A process for imparting hydrophobicity to fillers of aluminium trihydrate filler, said method including the step of mixing said fillers with a silane mixture composed of at least one mildly hydrophobic silane, at least one strongly hydrophobic silane, and at least one cross-linking epoxy-functional silane, at controlled alkaline pH.

25

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2008/001666

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C08K 9/06 (2006.01) **C08L 83/04** (2006.01)
C08L 63/00 (2006.01) **C08L 91/06** (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI, EPODOC, USPTO, CAPLUS: & keywords: silica, filler, hydrophob, silane, epoxy, wax, silicone oil, siloxane, PTFE, aluminium trihydrate or hydroxide, & similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/017700 A1 (UNIVERSITY OF SUNDERLAND) 15 February 2007 See the abstract, claims, examples, page 19	1, 3, 5-7, 9, 10, 17-25
X	GB 2433497 A (DOW CORNING CORPORATION) 27 June 2007 See paragraph [0025, claims	1, 3, 5-7, 10, 17-25, 30, 31, 34, 35
X	US 6420456 B1 (KOSKI) 16 July 2002 See columns 8, 10-12, claims	1-27

Further documents are listed in the continuation of Box C

See patent family annex

<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search
3 February 2009

Date of mailing of the international search report
11 FEB 2009

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2008/001666

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/0134950 A1 (KUDO et al) 17 July 2003 See the examples, claims	1-27
X	US 2005/0143282 A1 (CREUTZ et al) 30 June 2005 See paragraph [0016]	37-39, 47, 48
X	US 2005/0163738 A1 (LOIFENFELD et al) 28 July 2005 See the examples, claims	37-39, 47, 48
X	US 6040278 A (KOK et al) 21 March 2000 See the examples	37-39, 47, 48
X	US 5476884 A (KAYABA et al) 19 December 1995 See columns 3-6, table 5	6, 10, 11, 25-36, 43-47, 52, 53, 55-57
Y	See the whole document	54
X	US 5739186 A (HAYAKAWA et al) 14 April 1998 See columns 6, 7, examples	55-57
X	US 5306747 A (ITO et al) 26 April 1994 See columns 7, 8, examples	52, 53, 55-57
Y	KOVACH, G., "Release Agents", Encyclopedia of Polymer Science and Technology (edited by Mark, H. F., et al), 1970, vol 12, pages 57-65	53-57
Y	US 4218360 A (BURHANS et al) 19 August 1980 See the abstract, claims	53-57
X	US 5250637 A (SHIOBARA et al) 5 October 1993 See example 10	55-57
Y	See example 10	53-57

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2008/001666

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2008/001666

Supplemental Box

(To be used when the space in any of Boxes I to IV is not sufficient)

Continuation of Box No: III

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

In assessing whether there is more than one invention claimed, I have given consideration to those features which can be considered to potentially distinguish the claimed combination of features from the prior art. Where different claims have different distinguishing features they define different inventions.

This International Searching Authority has found that there are different inventions as follows:

- Claims 1-36, 40-46, 58 are directed to a process for imparting hydrophobicity to particles. It is considered that mixing the particles with a mixture of silanes at alkaline pH comprises a first distinguishing feature.
- Claims 37-39, 47-51, 52 (in part) are directed to a process for incorporating wax into silicone oil. It is considered that melting hydrophobic wax or waxes into silicone oil comprises a second distinguishing feature.
- Claims 52 (in part), 53 (in part) 54 (in part) are directed to a process for imparting hydrophobicity to insulators comprising epoxy resin/epoxy-functional silica blends. It is considered that adding hydrophobic epoxy-functional silanes to the blend or to the mould comprises a third distinguishing feature.
- Claims 53 (in part), 54 (in part), 56 (in part), 57 (in part) are directed to a process for imparting hydrophobicity to insulators comprising epoxy resin/epoxy-functional silica blends. It is considered that adding silicone oil to the blend or to the mould comprises a fourth distinguishing feature.
- Claims 55, 56 (in part), 57 (in part) are directed to a process for imparting hydrophobicity to insulators comprising epoxy resin/epoxy-functional silica blends. It is considered that adding wax or waxes to the blend comprises a fifth distinguishing feature.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

As discussed in the present specification (pages 1-21), it is known to impart hydrophobicity to fillers to alter the properties of the resultant products which incorporate the fillers; that addition of a hydrophobic filler to a polymer material will improve the material's hydrophobicity; and that hydrophobicity is a desirable property for insulators.

Therefore each of the abovementioned groups of claims has a different distinguishing feature and they do not share any feature which could satisfy the requirement for being a special technical feature. Because there is no common special technical feature it follows that there is no technical relationship between the identified inventions. Therefore the claims do not satisfy the requirement of unity of invention *a priori*.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2008/001666

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report	Patent Family Member			
WO 2007017700	AU 2006277712	AU 2006277713	CA 2617511	
	CA 2617513	CN 101242783	CN 101268155	
	EP 1919361	EP 1922367	US 2007187587	
	US 2007196656	WO 2007017701		
GB 2433497	NONE			
US 6420456	AU 75165/98	CA 2205789	CA 2288607	
	CN 1257524	EP 0983317	WO 9853004	
	ZA 9804299			
US 2003134950	EP 0959102	JP 2000044226	JP 2000108507	
	JP 2000109529	US 6521290	US 6855759	
US 2005143282	AU 2003219116	AU 2003232194	CN 1643126	
	CN 1646673	EP 1490470	EP 1499364	
	US 2005124530	WO 03082356	WO 03083031	
US 2005163738	BR PI0500242	DE 102004004155	EP 1559402	
	JP 2005213252			
US 6040278	BR 9803809	CA 2248489	CN 1228467	
	CZ 9803017	DE 19810031	EP 0942062	
	HU 9802133	JP 11293271	PL 328757	
US 5476884	EP 0384707	JP 2218735	JP 2218736	
US 5739186	EP 0705856	JP 8109242	JP 8109243	
	SG 41939			
US 5306747	JP 2011654	JP 2028213	US 5157061	
US 4218360	NONE			
US 5250637	JP 5152466			

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX